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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA

13 APR 1943

PART I ]

SECTION-A

[ VOL. XIII

## CONTENTS

No		PAGE
1	Motion in Incompressible Fluid of Variable Density <i>By Santi Ram Mukherjee</i>	1
2.	The Arms of a Spiral Nebula in Resisting Medium I <i>By Brij Basu Lal</i>	19
3	On the Theory of a Spiral Nebula II <i>By Brij Basu Lal</i>	28
4	Two Self-Reciprocal Functions <i>By H C Gupta</i>	37
5.	An Infinite Integral Involving Whittaker's Function <i>By R S Varma</i>	40
6.	On Self-Reciprocal Functions <i>By P C Mital</i>	42
7	Radial Oscillations of the Generalised Roche's Model <i>By H K Sen</i>	44
8	Chemical Examination of the Seeds of <i>Nigella sativa</i> , Linn. (Magrol). Part II The Component Glycerides of the Fatty Oil <i>By Bawa Kartar Singh and Ram Das Tewari</i>	54
9.	Studies on the Nature of Racemic Modifications of Optically Active Compounds in the Solid State. Part I <i>By Bawa Kartar Singh and Onkar Nath Puri</i>	59

February, 1943

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA

PART 2	SECTION A	VOLUME 13
--------	-----------	-----------

## CONTENTS

	PAGE
1. The Chemical Examination of the Fruits of <i>Terminalia Belerica</i> Roxb Part I The Component Acids of the Fatty Oil <i>By Brij Mohan Saran and Bawa Kartar Singh</i>	69
2. The Time of Setting and Changes in H-ion Concentration during the Setting of Nickel Hydroxide Gels Formed by the addition of Electrolytes to the Nickel Hydroxide Sol <i>By S D Mehta</i>	78
3. Chemical Examination of <i>Sphaeranthus Indicus</i> , Linn Part I—The Component Fatty Acids and Probable Glycerides of the Fatty Oil <i>By Bawa Kartar Singh and Ram Das Tiwari</i>	88
4. The Effect of H-ion Concentration on the Time of Setting and viscosity changes during the Setting of Thorium Arsenate Gel-Forming Mixtures <i>By T V Desai and S S Bhanage</i>	100
5. Chemical Examination of <i>Cassia Alata</i> Linn Part I The Component Acids of the Fatty Oil from the Seeds <i>By Bawa Kartar Singh and Ram Das Tiwari</i>	111
6. Chemical Examination of <i>Pinus Gerardiana</i> Wall The Component Fatty Acids and the Probable Glyceride Structure of the Fatty Oil from the Seeds <i>By Bawa Kartar Singh and Ram Das Tiwari</i>	120

**MARCH, 1943**

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# PROCEEDINGS

## OF THE

# NATIONAL ACADEMY OF SCIENCES

## INDIA

### 1943

---

PART 3]	SECTION A	[ VOL. 13
---------	-----------	-----------

---

### CONTENTS

No.		PAGE
1	Motion in Incompressible Fluid of Variable Density II <i>By Sanku Ram Mukherjee</i>	135
2.	Fluid Motions of the Type $\xi_1 = \lambda^2 u$ , etc and $\xi_2 = \lambda_1 u_1$ etc <i>By Ram Ballabh</i>	151
3.	The Rotating Cepheid <i>By H. K. Sen</i>	159
4.	The Arms of a Spiral Nebula in Resisting Medium II <i>By Brj Basu Lal</i>	165
5.	Some Infinite Integrals <i>By B. Mohan</i>	171
6.	Formation of the Arms of a Spiral Nebula <i>By Brj Basu Lal</i>	179
7.	Large Radial Oscillations of a Star <i>By H. K. Sen</i>	184

---

*May, 1943*

ALLAHABAD

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PROCEEDINGS  
OF THE  
NATIONAL ACADEMY OF SCIENCES  
INDIA  
1943

---

PART 4]

SECTION A

[ VOL 13

---

CONTENTS

	PAGE
On Waring's Problem ( <i>mod p</i> )	
<i>By Inder Chowla</i>	195
On Formulæ in Partitions and Divisors of a Number, Derived from Symmetric Functions	
<i>By M Ziaud Din</i>	221
Operational Calculus and Infinite Integrals	
<i>By H. C. Gupta</i>	225

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# PROCEEDINGS

## OF THE

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## INDIA

### 1943

---



---

PART 5]

SECTION A

[ VOL. 13

---



---

### CONTENTS

	PAGE
The Partial Pressures of Atoms and Molecules in the Saturated Vapours of the Alkali Elements	
<i>By A. S. Bhatnagar</i>	233
The Thermal Ionization of Sodium and Potassium Atoms	
<i>By A. S. Bhatnagar</i>	243
Structure of Liquid $\text{PCl}_5$	
<i>By Bishambhar Dayal Saksena</i>	251
The Crystal Structures and the Space Groups of Some Aromatic Crystals I. Phloroglucinol Dihydrate, $s\text{-C}_6\text{H}_3(\text{OH})_3 \cdot 2\text{H}_2\text{O}$	
<i>By S. L. Chorghade</i>	261

---

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# PROCEEDINGS

## OF THE

# NATIONAL ACADEMY OF SCIENCES

## INDIA

### 1943

---

PART 6]	SECTION A	[ VOL 13
---------	-----------	----------

---

### CONTENTS

	PAGE
On the Differentiability of Step Functions	
<i>By P D Shukla</i>	271
Lattice Sums of Cubic Crystals	
<i>By Rama Dhar Misra</i>	275
Intensity Calculations for the Fine Structure of Hydrogenic Atoms Part I	
<i>By K Basu</i>	284

---

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA (SECTION A)

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Part I]

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[Volume 13

## MOTION IN INCOMPRESSIBLE FLUID OF VARIABLE DENSITY

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MATHEMATICS DEPARTMENT, ALI AHABAD UNIVERSITY

Communicated by Prof A C Banerji

(Received on 2nd April, 1942)

Motion in incompressible viscous fluid has been investigated by various workers. Oseen and others have investigated the uniform motion of a sphere<sup>1</sup> and an ellipsoid<sup>2</sup> through a uniform viscous liquid and also calculated the resistance experienced by these bodies. Bairstow,<sup>3</sup> Filon<sup>4</sup> and others<sup>5</sup> have treated the problems of the steady translation of circular and elliptic cylinders and cylinders of arbitrary cross section<sup>6</sup> in a uniform viscous liquid and found the resistance in these cases. In this paper motion in viscous liquid of variable density has been discussed and solutions of hydrodynamical equations arising out of motion have been obtained in series. Three cases, where density  $\rho$  is given by (i)  $\rho = \frac{\rho_0}{1 + \lambda x}$ , (ii)  $\rho = \rho_0 (1 + \lambda x)$  and (iii)  $\rho = \rho_0 e^{-\lambda x}$ ,  $\lambda$  being a constant and  $\rho_0$ , the value of  $\rho$  at the origin, have been treated. It is believed that motion in viscous liquid of variable density has not been considered before.

Neglecting extraneous forces, when the fluid is incompressible the equations of motion are

$$\rho \frac{Du}{Dt} = - \frac{\partial p}{\partial x} + \mu \nabla^2 u$$

$$\rho \frac{Dv}{Dt} = - \frac{\partial p}{\partial y} + \mu \nabla^2 v$$

$$\rho \frac{Dw}{Dt} = - \frac{\partial p}{\partial z} + \mu \nabla^2 w$$

with  $\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$ , where  $\mu$  is constant and  $\rho$  variable.

Following Oseen,<sup>7</sup> we write  $\dot{U} + u$  for  $u$  and neglect terms of the second order in  $u$ ,  $v$  and  $w$ . These latter symbols now denote the components of the velocity which would remain if a translation— $\dot{U}$  were superposed on the whole system. The hydrodynamical equations accordingly take the forms

$$\left. \begin{aligned} U \frac{\partial u}{\partial x} &= -\frac{1}{\rho} \frac{\partial p}{\partial x} + \frac{\mu}{\rho} \nabla^2 u \\ U \frac{\partial v}{\partial x} &= -\frac{1}{\rho} \frac{\partial p}{\partial y} + \frac{\mu}{\rho} \nabla^2 v \\ U \frac{\partial w}{\partial x} &= -\frac{1}{\rho} \frac{\partial p}{\partial z} + \frac{\mu}{\rho} \nabla^2 w \\ \text{with } \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0 \end{aligned} \right\} \quad (A)$$

Case I

$$\rho = \rho_0 / (1 + \lambda x)$$

The equations (A) then become

$$\left. \begin{aligned} U \frac{\partial u}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial x} + \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 u \\ U \frac{\partial v}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial y} + \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 v \\ U \frac{\partial w}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial z} + \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 w \\ \text{with } \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0 \end{aligned} \right\} \quad (A_1)$$

Let  $u = u_1 + u_2$ ,  $v = v_1 + v_2$ , and  $w = w_1 + w_2$ , such that

$$\left. \begin{aligned} U \frac{\partial u_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial x} + \mu \frac{1+\lambda x}{\rho_0} \nabla^2 u_1 - \frac{\lambda}{\rho_0} p \\ U \frac{\partial v_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial y} + \mu \frac{1+\lambda x}{\rho_0} \nabla^2 v_1 \\ U \frac{\partial w_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial z} + \mu \frac{1+\lambda x}{\rho_0} \nabla^2 w_1 \\ \text{with } \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} &= 0 \end{aligned} \right\} \quad (A'_1)$$

and

$$\left. \begin{aligned} U \frac{\partial u_2}{\partial x} &= \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 u_2 + \frac{\lambda}{\rho_0} p \\ U \frac{\partial v_2}{\partial x} &= \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 v_2 \\ U \frac{\partial w_2}{\partial x} &= \frac{\mu(1+\lambda x)}{\rho_0} \nabla^2 w_2 \\ \text{with } \frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial w_2}{\partial z} &= 0 \end{aligned} \right\} \quad (A''_1)$$

Let us first consider ( $A'_1$ )

If there be a velocity potential  $\Phi$  such that

$$u_1 = -\frac{\partial \Phi}{\partial x}, \quad v_1 = -\frac{\partial \Phi}{\partial y} \quad \text{and} \quad w_1 = -\frac{\partial \Phi}{\partial z}$$

we get the modified form of ( $A'_1$ ) to be

$$\left. \begin{aligned} U \frac{\partial u_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial r} - \frac{\lambda}{\rho_0} p \\ U \frac{\partial v_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial y} \\ U \frac{\partial w_1}{\partial x} &= -\frac{1+\lambda x}{\rho_0} \frac{\partial p}{\partial z} \end{aligned} \right\}$$

with  $\nabla^2 \Phi = 0$  (1)

provided 
$$\frac{1+\lambda x}{\rho_0} p = U \frac{\partial \Phi}{\partial x} \quad (2)$$

Now for  $u_2$ ,  $v_2$  and  $w_2$  we consider ( $A''_1$ )

We can write ( $A''_1$ ) in the form

$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 u_2 - 2k_1 \frac{\partial u_2}{\partial x} \end{aligned} \right\} &= -\frac{\lambda}{\mu} p \\ \left\{ \begin{aligned} (1+\lambda x) \nabla^2 v_2 - 2k_1 \frac{\partial v_2}{\partial x} \end{aligned} \right\} &= 0 \\ \left\{ \begin{aligned} (1+\lambda x) \nabla^2 w_2 - 2k_1 \frac{\partial w_2}{\partial x} \end{aligned} \right\} &= 0$$

with  $\frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial w_2}{\partial z} = 0$ , where  $2k_1 = \frac{U\rho_0}{\mu}$

Since the vortea lines must be circles having the axis of  $x$  as a common axis, we may assume

$$\xi = 0, \quad \eta = -\frac{\partial \chi}{\partial x}, \quad \zeta = \frac{\partial \chi}{\partial y} \quad (3)$$

where  $\chi$  is a function of  $x$  and  $\omega$  (the distance from the axis of  $x$  only)

Now 
$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial r} \end{aligned} \right\} \frac{\partial w_2}{\partial x} + \lambda \nabla^2 w_2 = 0$$

$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \end{aligned} \right\} \frac{\partial v_2}{\partial x} + \lambda \nabla^2 v_2 = 0$$

$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \end{aligned} \right\} \frac{\partial u_2}{\partial y} = -\frac{\lambda}{\mu} \frac{\partial p}{\partial y}$$

$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \end{aligned} \right\} \frac{\partial u_2}{\partial x} = -\frac{\lambda}{\mu} \frac{\partial p}{\partial x}$$

$$\left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \end{aligned} \right\} \frac{\partial v_2}{\partial x} = 0 \quad \text{and} \quad \left\{ \begin{aligned} (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \end{aligned} \right\} \frac{\partial w_2}{\partial y} = 0$$



We know

$$\xi = \frac{\partial w_1}{\partial y} - \frac{\partial v_1}{\partial x}, \eta = \frac{\partial u_1}{\partial x} - \frac{\partial w_1}{\partial x} \text{ and } \zeta = \frac{\partial v_1}{\partial x} - \frac{\partial u_1}{\partial y}$$

$$\left\{ (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right\} \left( \frac{\partial u_1}{\partial x} - \frac{\partial w_1}{\partial x} \right) = -\frac{\lambda}{\mu} \frac{\partial p}{\partial x} + \lambda \nabla^2 v_1$$

$$\left\{ (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right\} \left( \frac{\partial v_1}{\partial x} - \frac{\partial u_1}{\partial y} \right) = \frac{\lambda}{\mu} \frac{\partial p}{\partial y} - \lambda \nabla^2 v_1$$

so that

$$\left\{ (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right\} \eta = \lambda \nabla^2 v_1 - \frac{\lambda}{\mu} \frac{\partial p}{\partial x} \quad (4)$$

$$\left\{ (1+\lambda x) \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right\} \zeta = -\lambda \nabla^2 v_1 + \frac{\lambda}{\mu} \frac{\partial p}{\partial y} \quad (5)$$

$$\begin{aligned} \text{Now } \frac{\partial \eta}{\partial x} - \frac{\partial \zeta}{\partial y} &= \frac{\partial}{\partial x} \left( \frac{\partial u_1}{\partial x} - \frac{\partial w_1}{\partial x} \right) - \frac{\partial}{\partial y} \left( \frac{\partial v_1}{\partial x} - \frac{\partial u_1}{\partial y} \right) \\ &= \frac{\partial^2 u_1}{\partial x^2} - \frac{\partial^2 w_1}{\partial x \partial x} - \frac{\partial^2 v_1}{\partial y \partial x} + \frac{\partial^2 u_1}{\partial y^2} \\ &= \frac{\partial^2 u_1}{\partial x^2} + \frac{\partial^2 u_1}{\partial y^2} - \frac{\partial}{\partial x} \left( \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial x} \right) \\ &= \frac{\partial^2 u_1}{\partial x^2} + \frac{\partial^2 u_1}{\partial y^2} - \frac{\partial}{\partial x} \left( -\frac{\partial u_1}{\partial x} \right), \text{ since } \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial x} = 0 \\ &= \nabla^2 u_1 \end{aligned}$$

$$\text{Similarly, } \frac{\partial \zeta}{\partial x} - \frac{\partial \xi}{\partial y} = \nabla^2 v_1 \text{ and } \frac{\partial \xi}{\partial y} - \frac{\partial \eta}{\partial x} = \nabla^2 w_1$$

Hence, substituting the values of  $\nabla^2 w_1$  and  $\nabla^2 v_1$  in (4) and (5), we get

$$\begin{aligned} \left\{ (1+\lambda x) \nabla^2 + (\lambda - 2k_1) \frac{\partial}{\partial x} \right\} \eta &= -\frac{\lambda}{\mu} \frac{\partial p}{\partial x} \\ \left\{ (1+\lambda x) \nabla^2 + (\lambda - 2k_1) \frac{\partial}{\partial x} \right\} \zeta &= \frac{\lambda}{\mu} \frac{\partial p}{\partial y} \text{ since } \xi = 0 \text{ by (3)} \end{aligned}$$

Now substituting the values of  $\eta$  and  $\zeta$  from (3) in the above equations, we get the equation to determine  $\chi$  to be

$$\left\{ (1+\lambda x) \nabla^2 + (\lambda - 2k_1) \frac{\partial}{\partial x} \right\} \chi = \frac{\lambda}{\mu} p \quad (6)$$

an additive function of  $x$  only being obviously irrelevant.

Hence,

$$\begin{aligned}
 2k_1 \frac{\partial u_2}{\partial x} &= (1 + \lambda x) \nabla^2 u_2 + \frac{\lambda}{\mu} p \\
 &= \frac{\lambda}{\mu} p + (1 + \lambda x) \left( \frac{\partial \eta}{\partial x} - \frac{\partial \xi}{\partial y} \right) \\
 &= \frac{\lambda}{\mu} p - (1 + \lambda x) \left( \frac{\partial^2 \chi}{\partial y^2} + \frac{\partial^2 \chi}{\partial z^2} \right) \\
 &= (1 + \lambda x) \frac{\partial^2 \chi}{\partial x^2} + (\lambda - 2k_1) \frac{\partial \chi}{\partial x}, \quad \text{by (6)}
 \end{aligned}$$

$$\begin{aligned}
 2k_1 \frac{\partial v_2}{\partial x} &= (1 + \lambda x) \nabla^2 v_2 \\
 &= (1 + \lambda x) \left( \frac{\partial \xi}{\partial x} - \frac{\partial \xi}{\partial x} \right) \\
 &= (1 + \lambda x) \frac{\partial^2 \chi}{\partial x \partial y}
 \end{aligned}$$

$$\begin{aligned}
 2k_1 \frac{\partial w_2}{\partial x} &= (1 + \lambda x) \nabla^2 w_2 \\
 &= (1 + \lambda x) \left( \frac{\partial \xi}{\partial y} - \frac{\partial \eta}{\partial x} \right) \\
 &= (1 + \lambda x) \frac{\partial^2 \chi}{\partial x \partial z}
 \end{aligned}$$

So that

$$\begin{aligned}
 u_2 &= \frac{1}{2k_1} (1 + \lambda x) \frac{\partial \chi}{\partial x} - \chi \\
 v_2 &= \frac{1}{2k_1} (1 + \lambda x) \frac{\partial \chi}{\partial y} - \frac{\lambda}{2k_1} \int \frac{\partial \chi}{\partial y} dx \\
 w_2 &= \frac{1}{2k_1} (1 + \lambda x) \frac{\partial \chi}{\partial z} - \frac{\lambda}{2k_1} \int \frac{\partial \chi}{\partial z} dx
 \end{aligned}$$

Now we have to find the form of  $\chi$  given by (6)

$$\begin{aligned}
 (1 + \lambda x) \nabla^2 \chi + (\lambda - 2k_1) \frac{\partial \chi}{\partial x} &= \frac{\lambda}{\mu} p = \frac{\lambda}{\mu} \frac{U \rho_0}{1 + \lambda x} \frac{\partial \Phi}{\partial x} \quad \text{from (2)} \\
 &= \frac{2k_1 \lambda}{1 + \lambda x} \frac{\partial \Phi}{\partial x}
 \end{aligned}$$

where  $\nabla^2 \Phi = 0$  by (1)

Turning to the solution of the above equation, we find that since the problem is one of preferential motion along the axis of  $x$ , we are justified in considering the

solution of  $\nabla^2 \Phi = 0$  in the form  $\Phi = R \cdot S$ , where  $R$  is a function of  $x$  only and  $S$  that of  $w$  and  $\phi$  only, where  $w = \sqrt{y^2 + z^2}$  and  $\tan \phi = \frac{z}{y}$ , so that from  $\nabla^2 \Phi = 0$ , we get

$$S \frac{d^2 R}{dx^2} + R \nabla_1^2 S = 0, \text{ where } \nabla_1^2 \equiv \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\text{or} \quad \frac{1}{R} \frac{d^2 R}{dx^2} + \frac{1}{S} \nabla_1^2 S = 0$$

This is satisfied if we write

$$\frac{d^2 R}{dx^2} - kR = 0 \text{ and } \nabla_1^2 S + kS = 0, \text{ where } k \text{ is an arbitrary constant}$$

Whereby  $R = c_1 e^{\sqrt{k}x} + c_2 e^{-\sqrt{k}x}$ ,  $c_1$  and  $c_2$  being arbitrary constants

$$\text{and} \quad S^{(8)} = B'_n J_n(\beta_1 \omega) \frac{\cos}{\sin} \left\} n\phi, \text{ if } k = \beta_1^2\right.$$

$$\text{or} \quad B'_m I_m(\beta_2 \omega) \frac{\cos}{\sin} \left\} m\phi, \text{ if } k = -\beta_2^2\right.$$

In the differential equation for  $\chi$  we put  $\chi = VS$ , where  $V$  is a function of  $x$  only, so that

$$\frac{\partial \chi}{\partial x} = S \frac{\partial V}{\partial x}, \quad \frac{\partial^2 \chi}{\partial x^2} = S \frac{d^2 V}{dx^2} \text{ and } \nabla_1^2 \chi = V \nabla_1^2 S = -kVS$$

Then we get

$$S \left[ (1 + \lambda x) \left( \frac{d^2 V}{dx^2} - kV \right) + (\lambda - 2k_1) \frac{dV}{dx} \right] = \frac{2k_1 \lambda}{1 + \lambda x} \frac{dR}{dx} S$$

So that  $V$  is to be determined from

$$(1 + \lambda x) \left( \frac{d^2 V}{dx^2} - kV \right) + (\lambda - 2k_1) \frac{dV}{dx} = \frac{2k_1 \lambda}{1 + \lambda x} \frac{dR}{dx},$$

$$\text{where } R = c_1 e^{\sqrt{k}x} + c_2 e^{-\sqrt{k}x}$$

Put  $1 + \lambda x = \lambda x_1$  so that  $\delta x = \delta x_1$

$$\text{Hence, } \lambda x_1 \left( \frac{d^2 V}{dx_1^2} - kV \right) + (\lambda - 2k_1) \frac{dV}{dx_1} = \frac{2k_1 \lambda}{\lambda x_1} \frac{dR}{dx_1}$$

$$\text{or } x_1 \left( \frac{d^2 V}{dx_1^2} - kV \right) + \frac{\lambda - 2k_1}{\lambda} \frac{dV}{dx_1} = \frac{2k_1}{\lambda} \frac{1}{x_1} \frac{dR}{dx_1}$$

$$\text{or } x_1 \frac{d^2 V}{dx_1^2} + a \frac{dV}{dx_1} - kx_1 V = \frac{b}{x_1} \frac{dR}{dx_1}, \text{ where } a = \frac{\lambda - 2k_1}{\lambda} \text{ and } b = \frac{2k_1}{\lambda}$$

$$\text{Let us first solve } x_1 \frac{d^2 V}{dx_1^2} + a \frac{dV}{dx_1} - kx_1 V = 0$$

$$\text{Let } V = \sum_{j=1}^{\infty} A_j x_1^{m_j} \equiv A_1 x_1^{m_1} + A_2 x_1^{m_2} + \dots + A_j x_1^{m_j} + \dots$$

Substituting for  $V$  we get

$$\left. \begin{aligned} & A_1 m_1 (m_1 + a - 1) x_1^{m_1-1} - A_1 k x_1^{m_1+1} \\ & + A_2 m_2 (m_2 + a - 1) x_1^{m_2-1} - A_2 k x_1^{m_2+1} \\ & + A_3 m_3 (m_3 + a - 1) x_1^{m_3-1} - A_3 k x_1^{m_3+1} \\ & + A_{s-1} m_{s-1} (m_{s-1} + a - 1) x_1^{m_{s-1}-1} - A_{s-1} k x_1^{m_{s-1}+1} \\ & + A_s m_s (m_s + a - 1) x_1^{m_s-1} - A_s k x_1^{m_s+1} \\ & + \\ & + \end{aligned} \right\} \equiv 0 \quad (7)$$

From (7) we get  $m_1 (m_1 + a - 1) = 0$   $m_1 = 0$  or  $1 - a$

$$m_2 - 1 = m_1 + 1 \text{ or } m_2 = m_1 + 2$$

$$m_3 = m_2 + 2$$

$$= m_1 + 4$$

$$m_s = m_1 + 2(s-1)$$

and  $A_{s-1} k = A_s m_s (m_s + a - 1)$  for  $s \geq 2$

$$\text{or } \frac{A_s x_1^s}{A_{s-1}} = \frac{k x_1^s}{m_s (m_s + a - 1)} = \frac{k x_1^s}{(m_1 + 2s - 2)(m_1 + 2s + a - 3)}$$

$$\rightarrow 0 \text{ as } s \rightarrow \infty$$

Hence, the series thus found is absolutely and uniformly Convergent for all values of  $x_1$

Now the roots of  $m_1$  are zero and  $1 - a$

$$1 - a = 1 - \frac{\lambda - 2k_1}{\lambda} = \frac{2k_1}{\lambda} \text{ If } \frac{2k_1}{\lambda} \text{ be not an integer, either positive or}$$

negative, we get two independent series for  $m_1 = 0$  and  $\frac{2k_1}{\lambda}$ ,  $k_1$  obviously is not zero.

If  $\frac{2k_1}{\lambda}$  happens to be an integer other than unity, the solutions in that case

$$\text{will be } \left[ V \right]_{m_1 = \frac{2k_1}{\lambda}} \text{ and } \left[ \frac{\partial V}{\partial m_1} \right]_{m_1 = 0}.$$

Again, if  $\lambda = 2k_1$ , our equation will reduce to

$$\frac{d^2 V}{dx_1^2} - KV = \frac{b}{x_1^2} \frac{dR}{dx_1},$$

whereby the solutions can be easily found

$$\begin{aligned} A_s &= \frac{h}{(m_1 + 2s - 2)(m_1 + 2s + a - 3)} A_{s-1}, \text{ for } s \geq 2 \\ A_2 &= \frac{h}{(m_1 + 2)(m_1 + a + 1)} A_1, A_3 = \frac{h}{(m_1 + 4)(m_1 + a + 3)} A_2 \\ &= \frac{h^2}{(m_1 + 4)(m_1 + 2)(m_1 + a + 3)(m_1 + a + 1)} A_1 \\ A_4 &= \frac{h^3}{(m_1 + 6)(m_1 + 4)(m_1 + 2)(m_1 + a + 5)(m_1 + a + 3)(m_1 + a + 1)} A_1, \text{ etc} \end{aligned}$$

Hence,

$$V = A_1 x_1^{m_1} \left[ 1 + \frac{h x_1^2}{(m_1 + 2)(m_1 + a + 1)} + \frac{h^2 x_1^4}{(m_1 + 4)(m_1 + 2)(m_1 + a + 3)(m_1 + a + 1)} + \frac{h^3 x_1^6}{(m_1 + 6)(m_1 + 4)(m_1 + 2)(m_1 + a + 5)(m_1 + a + 3)(m_1 + a + 1)} + \dots \right],$$

where  $A_1$  is an arbitrary constant

For the particular Integrals we write the equation as

$$\frac{d^2 V}{dx_1^2} + \frac{a}{x_1} \frac{dV}{dx_1} - kV = \frac{b}{x_1^2} \frac{dR}{dx_1}$$

The complete solution is given by (9)  $V = BV + AV$ ,

where

$$\left. \begin{aligned} A &= E + \int \frac{b}{x_1^2} \frac{dR}{dx_1} V_1 e^{\int \frac{a}{x_1} dx_1} dx_1 \\ B &= F - \int \frac{b}{x_1^2} \frac{dR}{dx_1} V_2 e^{\int \frac{a}{x_1} dx_1} dx_1 \end{aligned} \right\}, \text{ E, F being arbitrary constants}$$

Now let us consider the integrals contained in A and B. After substituting for R we find that they are of the form —

$$b\sqrt{k} \int \frac{1}{x_1^2} \left( c_1 x_1 e^{\sqrt{k} x_1} - c_2 x_1 e^{-\sqrt{k} x_1} \right) x_1^a V_q dx_1, \text{ where } q=1 \text{ or } 2.$$

Thus we see, we have to evaluate integrals of the form

$$\int e^{a_1 x} x^{b_1} dx, \text{ if } k \text{ is positive}$$

$$\text{and } \int \frac{\cos}{\sin} \left\{ a_1 x, x^{b_1} \right\} dx, \text{ if } k \text{ is negative}$$

$$\text{or } \int e^{a_1 x} x^{b_1} \log x dx \text{ and } \int \frac{\cos}{\sin} \left\{ a_1 x, x^{b_1} \right\} \log x dx$$

But the above forms are integrable. Hence, the solution of V can be obtained

Again,  $\chi = VS$  and since  $\chi$  is a function of  $x$  and  $\omega$  only,  $S$  must be independent of  $\phi$ . Hence,  $S$  is a function of  $\omega$  only. Hence the equation for  $S$  becomes

$$\frac{d^2 S}{d\omega^2} + \frac{1}{\omega} \frac{dS}{d\omega} + KS = 0$$

$$\left. \begin{array}{l} \text{whereby } S = A_0 J_0(\beta_1 \omega) \\ \text{or } B_0 I_0(\beta_1 \omega) \end{array} \right\}$$

Thus  $\chi$  has been found. Again  $\Phi$  is given by  $\Phi = RS$ . Hence, we can find the value of  $p$  from (2), since  $\Phi$  is known. Substituting the value of  $\chi_1, u_2, v_2$  and  $w_2$  can be determined and  $\Phi$  being known, we can get  $u_1, v_1$  and  $w_1$ . Thus a complete solution of the problem has been determined.

## CASE II

$$\rho = \rho_0 (1 + \lambda x)$$

The equations of motion become

$$\left. \begin{array}{l} \text{I} \quad \frac{\partial u}{\partial x} = - \frac{1}{\rho_0 (1 + \lambda x)} \frac{\partial p}{\partial x} + \frac{\mu}{\rho_0 (1 + \lambda x)} \nabla^2 u \\ \text{II} \quad \frac{\partial v}{\partial x} = - \frac{1}{\rho_0 (1 + \lambda x)} \frac{\partial p}{\partial y} + \frac{\mu}{\rho_0 (1 + \lambda x)} \nabla^2 v \\ \text{III} \quad \frac{\partial w}{\partial x} = - \frac{1}{\rho_0 (1 + \lambda x)} \frac{\partial p}{\partial z} + \frac{\mu}{\rho_0 (1 + \lambda x)} \nabla^2 w \\ \text{with } \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \end{array} \right\} \quad (A_1)$$

$$\text{or} \quad \left. \begin{array}{l} \rho_0 U (1 + \lambda x) \frac{\partial u}{\partial x} = - \frac{\partial p}{\partial x} + \mu \nabla^2 u \\ \rho_0 U (1 + \lambda x) \frac{\partial v}{\partial x} = - \frac{\partial p}{\partial y} + \mu \nabla^2 v \\ \rho_0 U (1 + \lambda x) \frac{\partial w}{\partial x} = - \frac{\partial p}{\partial z} + \mu \nabla^2 w \\ \text{with } \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \end{array} \right\}$$

Let  $u = u_1 + u_2$ ,  $v = v_1 + v_2$  and  $w = w_1 + w_2$ , such that

$$\left. \begin{array}{l} \rho_0 U (1 + \lambda x) \frac{\partial u_1}{\partial x} + \rho_0 U \lambda u_1 = - \frac{\partial p}{\partial x} + \mu \nabla^2 u_1 \\ \rho_0 U (1 + \lambda x) \frac{\partial v_1}{\partial x} = - \frac{\partial p}{\partial y} + \mu \nabla^2 v_1 \\ \rho_0 U (1 + \lambda x) \frac{\partial w_1}{\partial x} = - \frac{\partial p}{\partial z} + \mu \nabla^2 w_1 \\ \text{with } \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0 \end{array} \right\} \quad (A_1')$$

$$\text{and} \quad \left. \begin{aligned} \rho_0 U (1 + \lambda x) \frac{\partial w_2}{\partial x} - \rho_0 U \lambda w_1 &= \mu \nabla^2 w_2 \\ \rho_0 U (1 + \lambda x) \frac{\partial w_2}{\partial x} &= \mu \nabla^2 w_2 \\ \rho_0 U (1 + \lambda x) \frac{\partial w_2}{\partial x} &= \mu \nabla^2 w_2 \end{aligned} \right\} \quad (A_2'')$$

with  $\frac{\partial w_2}{\partial x} + \frac{\partial w_2}{\partial y} + \frac{\partial w_2}{\partial z} = 0$

First we consider the equations  $(A_2')$ .

If there be a velocity potential  $\Phi$  such that

$$u_1 = -\frac{\partial \Phi}{\partial x}, \quad v_1 = -\frac{\partial \Phi}{\partial y} \quad \text{and} \quad w_1 = -\frac{\partial \Phi}{\partial z},$$

we get the modified form of  $(A_2')$  to be

$$\begin{aligned} \rho_0 U (1 + \lambda x) \frac{\partial w_1}{\partial x} + \rho_0 U \lambda w_1 &= -\frac{\partial p}{\partial x} \\ \rho_0 U (1 + \lambda x) \frac{\partial w_1}{\partial x} &= -\frac{\partial p}{\partial y} \\ \rho_0 U (1 + \lambda x) \frac{\partial w_1}{\partial x} &= -\frac{\partial p}{\partial z} \end{aligned}$$

with  $\nabla^2 \Phi = 0$

provided  $\rho = \rho_0 U (1 + \lambda x) \frac{\partial \Phi}{\partial x}$

Now for  $u_2, v_2$  and  $w_2$ . We consider  $(A_2'')$

We can write  $(A_2'')$  in the form

$$\begin{aligned} \left( \frac{1}{1 + \lambda x} \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) w_2 &= -2k_1 \lambda \frac{w_1}{1 + \lambda x} \\ \left( \frac{1}{1 + \lambda x} \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) w_2 &= 0 \\ \left( \frac{1}{1 + \lambda x} \nabla^2 - 2k_1 \frac{\partial}{\partial x} \right) w_2 &= 0 \end{aligned}$$

with  $\frac{\partial w_2}{\partial x} + \frac{\partial w_2}{\partial y} + \frac{\partial w_2}{\partial z} = 0$ , where  $2k_1 = \frac{U \rho_0}{\mu}$

Since the vortex lines must be circles having the axis of  $z$  as a common axis, we may assume

$$\xi = 0, \quad \eta = -\frac{\partial X}{\partial x}, \quad \zeta = \frac{\partial X}{\partial y} \quad (3.1)$$

where  $X$  is a function of  $x$  and  $\omega$  (the distance from the axis of  $z$ ) only

Proceeding, as in Case I, we get

$$\left[ \frac{1}{1+\lambda x} \nabla^2 + \left\{ \frac{\lambda}{(1+\lambda x)^2} - 2k_1 \right\} \frac{\partial}{\partial x} \right] \eta = - \frac{2k_1 \lambda}{1+\lambda x} \frac{\partial u_1}{\partial x}$$

$$\left[ \frac{1}{1+\lambda y} \nabla^2 + \left\{ \frac{\lambda}{(1+\lambda y)^2} - 2k_1 \right\} \frac{\partial}{\partial y} \right] \zeta = \frac{2k_1 \lambda}{1+\lambda x} \frac{\partial u_1}{\partial y}$$

$$\text{whereby} \quad \left[ \frac{1}{1+\lambda x} \nabla^2 + \left\{ \frac{\lambda}{(1+\lambda x)^2} - 2k_1 \right\} \frac{\partial}{\partial x} \right] \chi = \frac{2k_1 \lambda}{1+\lambda x} u_1, \quad (6.1)$$

an additive function of  $x$  only being obviously irrelevant

$$\begin{aligned} 2k_1 \frac{\partial u_1}{\partial x} &= - \frac{1}{1+\lambda x} \nabla^2 u_1 + 2k_1 \lambda \frac{u_1}{1+\lambda x} \\ &= 2k_1 \lambda \frac{u_1}{1+\lambda x} + \frac{1}{1+\lambda x} \left( \frac{\partial \eta}{\partial x} - \frac{\partial \zeta}{\partial y} \right) \\ &= 2k_1 \lambda \frac{u_1}{1+\lambda x} - \frac{1}{1+\lambda x} \left( \frac{\partial^2 \chi}{\partial y^2} + \frac{\partial^2 \chi}{\partial x^2} \right) \\ &= \frac{1}{1+\lambda x} \frac{\partial^2 \chi}{\partial x^2} + \left\{ \frac{\lambda}{(1+\lambda x)^2} - 2k_1 \right\} \frac{\partial \chi}{\partial x} \quad \text{by (6.1)} \\ 2k_1 \frac{\partial v_1}{\partial y} &= \frac{1}{1+\lambda y} \nabla^2 v_1 = \frac{1}{1+\lambda x} \left( \frac{\partial \zeta}{\partial x} - \frac{\partial \xi}{\partial y} \right) \\ &= \frac{1}{1+\lambda x} \frac{\partial^2 \chi}{\partial x \partial y}, \quad \text{since } \xi = 0 \\ 2k_1 \frac{\partial w_1}{\partial x} &= \frac{1}{1+\lambda y} \nabla^2 w_1 = \frac{1}{1+\lambda x} \left( \frac{\partial \xi}{\partial y} - \frac{\partial \eta}{\partial x} \right) \\ &= - \frac{1}{1+\lambda x} \frac{\partial^2 \chi}{\partial x \partial y} \end{aligned}$$

so that

$$\begin{aligned} u_1 &= \frac{1}{2k_1} \left[ \frac{1}{1+\lambda x} \frac{\partial \chi}{\partial x} - 2k_1 \chi + \frac{2\lambda}{(1+\lambda x)^2} \chi + 4\lambda^2 \int \frac{\chi}{(1+\lambda x)} dx \right] \\ v_1 &= \frac{1}{2k_1} \left[ \frac{1}{1+\lambda x} \frac{\partial \chi}{\partial y} + \int \frac{\lambda}{(1+\lambda x)^2} \frac{\partial \chi}{\partial y} dx \right] \\ w_1 &= \frac{1}{2k_1} \left[ \frac{1}{1+\lambda x} \frac{\partial \chi}{\partial x} + \int \frac{\lambda}{(1+\lambda x)^2} \frac{\partial \chi}{\partial x} dx \right] \end{aligned}$$

Now let us turn to (6.1) which may be written as

$$(1+\lambda x) \nabla^2 \chi + \left\{ \lambda - 2k_1 (1+\lambda x)^2 \right\} \frac{\partial \chi}{\partial x} = - 2k_1 \lambda (1+\lambda x) \frac{\partial \Phi}{\partial x}, \quad \text{where } \nabla^2 \Phi = 0$$

Following the same argument, as in Case I, and writing

$$\Phi = RS, \quad \chi = VS \quad \text{and} \quad 1+\lambda x = \lambda x_1, \quad \text{where} \quad \frac{d^2 R}{dx^2} = \lambda R = 0 \quad \text{and} \quad \nabla_1^2 S + KS = 0,$$



we get the equation to determine  $V$  to be

$$x_1 \left( \frac{d^2 V}{dx_1^2} - KV \right) + \left( 1 - 2k_1 \lambda x_1^2 \right) \frac{dv}{dx_1} = -2k_1 \lambda x_1 \frac{dR}{dx_1}$$

Let us first get the Complementary function given by

$$x_1 \frac{d^2 V}{dx_1^2} + \left( 1 - 2k_1 \lambda x_1^2 \right) \frac{dv}{dx_1} - k_{s+1} V = 0$$

$$\text{Let } V = \sum_{s=1}^{\infty} \beta_s x_1^{m_s} \equiv \beta_1 x_1^{m_1} + \beta_2 x_1^{m_2} + \dots + \beta_s x_1^{m_s} + \dots$$

Substituting, we get

$$\left. \begin{aligned} & \beta_1 m_1^2 x_1^{m_1-1} - \beta_1 (2k_1 \lambda m_1 + k) x_1^{m_1+1} \\ & + \beta_2 m_2^2 x_1^{m_2-1} - \beta_2 (2k_1 \lambda m_2 + k) x_1^{m_2+1} \\ & + \beta_3 m_3^2 x_1^{m_3-1} - \beta_3 (2k_1 \lambda m_3 + k) x_1^{m_3+1} \\ & + \\ & + \\ & + \beta_{s-1} m_{s-1}^2 x_1^{m_{s-1}-1} - \beta_{s-1} (2k_1 \lambda m_{s-1} + k) x_1^{m_{s-1}+1} \\ & + \beta_s m_s^2 x_1^{m_s-1} - \beta_s (2k_1 \lambda m_s + k) x_1^{m_s+1} \\ & + \dots \end{aligned} \right\} \equiv 0$$

From this we get

$$\begin{aligned} m_1^2 &= 0, \quad \text{i.e., } m_1 = 0 \\ m_1 + 1 &= m_2 - 1 \quad \text{or } m_2 = m_1 + 2 \\ m_2 &= m_3 + 2 = m_1 + 4 \\ m_3 &= m_4 + 2 = m_1 + 6 \\ \beta_s m_s^2 - \beta_{s-1} (2k_1 \lambda m_{s-1} + k) &\text{ or } \frac{\beta_s x_1^s}{\beta_{s-1}} = \frac{2k_1 \lambda m_{s-1} + k}{m_{s-1}^2} x_1^2 \\ &= \frac{\{2k_1 \lambda (m_1 + 2s - 4) + k\}}{(m_1 + 2s - 2)^2} x_1^2 \end{aligned}$$

$$\longrightarrow 0 \text{ as } s \longrightarrow \infty$$

Hence, the series thus found is absolutely and uniformly Convergent for all values of  $x_1$ ,

Since the two values of  $m_1$  have coincided into one viz zero the solutions will be given by

$$\left[ V \right]_{m=0} = 0 \quad \text{and} \quad \left[ \frac{\partial V}{\partial m_1} \right]_{m=0}$$

by suitably modifying the arbitrary constant

$$\text{Now} \quad B = \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 2)^2} B_1 \quad \text{for } \lambda \geq 0$$

$$B_2 = \frac{{}^0k_1 \lambda m_1 + I}{(m_1 + 2)^2} B_1 \quad B_3 = \frac{{}^2I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} B_1 - \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} \frac{{}^1I_1 \lambda m_1 + I}{(m_1 + 2)^2} B_1$$

$$B_4 = \frac{{}^2I_1 \lambda (m_1 + 4) + I}{(m_1 + 6)^2} - \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} - \frac{{}^1I_1 \lambda m_1 + I}{(m_1 + 2)^2} B_1 \text{ etc}$$

Hence

$$V = B_1 x_1^{-1} \left[ 1 + \frac{{}^0I_1 \lambda m_1 + I}{(m_1 + 2)^2} x_1^2 + \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} \frac{{}^1I_1 \lambda m_1 + I}{(m_1 + 2)^2} x_1^4 \right. \\ \left. + \frac{{}^1I_1 \lambda (m_1 + 4) + I}{(m_1 + 6)^2} - \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} - \frac{{}^1I_1 \lambda m_1 + I}{(m_1 + 2)^2} x_1^2 + \dots \right]$$

where  $B_1$  is an arbitrary constant

$$\frac{\partial V}{\partial m_1} = V \log x_1 + B_1 x_1^{m_1+1} \left\{ \frac{{}^2I_1 \lambda m_1 + I}{(m_1 + 2)^2} \left( \frac{{}^0I_1 \lambda}{2I_1 \lambda m_1 + k} - m_1 + 2 \right) + \right. \\ \frac{{}^2I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} - \frac{{}^1I_1 \lambda m_1 + I}{(m_1 + 2)^2} \left\{ \frac{{}^1I_1 \lambda}{2I_1 \lambda (m_1 + 2) + k} + \frac{k_1 \lambda}{{}^1I_1 \lambda m_1 + I} - m_1 + 4 - \frac{2}{m_1 + 2} \right\} \\ x_1^2 + \frac{{}^2I_1 \lambda (m_1 + 4) + I}{(m_1 + 6)^2} - \frac{{}^1I_1 \lambda (m_1 + 2) + I}{(m_1 + 4)^2} - \frac{{}^2I_1 \lambda m_1 + I}{(m_1 + 2)^2} \left\{ \frac{{}^2I_1 \lambda}{I_1 \lambda (m_1 + 4) + I} \right. \\ \left. + 2k_1 \lambda \frac{{}^2I_1 \lambda}{(m_1 + 2) + k} + \frac{2k_1 \lambda}{2I_1 \lambda m_1 + I} - \frac{2}{m_1 + 6} - \frac{2}{m_1 + 4} - \frac{2}{m_1 + 2} \right\} x_1^4 + \dots \left. \right\}$$

so that

$$V_1 = \left[ V \right]_{m_1=0} \quad \text{and} \quad V_2 = \left[ \frac{\partial V}{\partial m_1} \right]_{m_1=0}$$

Hence the complete solution of (6.1) is given by

$$X = S (BV_1 + AV_2) \quad \text{where } S = A_0 J_0 (\beta_1 \omega), \text{ if } \beta_1^2 = k \\ \text{or } B_0 I_0 (\beta_2 \omega), \text{ if } \beta_2^2 = -k$$

$$\text{and } A = E - 2k_1 \lambda \int \frac{dR}{dx_1} V_1 e^{\int \frac{1 - k_1 \lambda x_1}{x_1} dx_1} dx_1 \quad \left\{ \begin{array}{l} E \text{ and } F \text{ being arbitrary} \\ \text{constants} \end{array} \right. \\ \text{and } B = F + 2k_1 \lambda \int \frac{dR}{dx_1} V_2 e^{\int \frac{1 - 2I_1 \lambda x_1}{x_1} dx_1} dx_1$$

The forms given in A and B are integrable as in Case I. Hence, we can have a complete solution of (A<sub>2</sub>)

### CASE III

$$\rho = \rho_0 e^{-\lambda x}$$

The equations of motion become

$$\left. \begin{aligned} \text{U} \frac{\partial u}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial x} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 u \\ \text{U} \frac{\partial v}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial y} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 v \\ \text{U} \frac{\partial w}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial z} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 w \\ \text{with } \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} &= 0 \end{aligned} \right\} \quad (A_3)$$

Let  $u = u_1 + u_2$ ,  $v = v_1 + v_2$  and  $w = w_1 + w_2$

such that

$$\left. \begin{aligned} \text{U} \frac{\partial u_1}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial x} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 u_1 - \frac{\lambda e^{\lambda x}}{\rho_0} p \\ \text{U} \frac{\partial v_1}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial y} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 v_1 \\ \text{U} \frac{\partial w_1}{\partial x} &= -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial z} + \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 w_1 \\ \text{with } \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} &= 0 \end{aligned} \right\} \quad (A'_1)$$

and

$$\left. \begin{aligned} \text{U} \frac{\partial u_2}{\partial x} &= \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 u_2 + \frac{\lambda e^{\lambda x}}{\rho_0} p \\ \text{U} \frac{\partial v_2}{\partial x} &= \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 v_2 \\ \text{U} \frac{\partial w_2}{\partial x} &= \frac{\mu e^{\lambda x}}{\rho_0} \nabla^2 w_2 \\ \text{with } \frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial w_2}{\partial z} &= 0 \end{aligned} \right\} \quad (A''_1)$$

First we consider (A'<sub>1</sub>)

If there be a velocity potential  $\Phi$ , such that

$$u_1 = -\frac{\partial \Phi}{\partial x}, \quad v_1 = -\frac{\partial \Phi}{\partial y} \quad \text{and} \quad w_1 = -\frac{\partial \Phi}{\partial z},$$

we get the modified form of ( $\Lambda'_1$ ) to be

$$U \frac{\partial w_1}{\partial z} = -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial z} - \frac{\lambda e^{\lambda x}}{\rho_0} p$$

$$U \frac{\partial v_1}{\partial x} = -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial y}$$

$$U \frac{\partial w_1}{\partial x} = -\frac{e^{\lambda x}}{\rho_0} \frac{\partial p}{\partial x}$$

$$\text{with } \nabla^2 \Phi = 0$$

provided

$$U \frac{\partial \Phi}{\partial x} = \frac{e^{\lambda x}}{\rho_0} p$$

We now write ( $\Lambda''_x$ ) in the form

$$\left( e^{\lambda x} \nabla^2 - 2h_1 \frac{\partial}{\partial x} \right) w_1 = -\frac{\lambda}{\mu} e^{\lambda x} p$$

$$\left( e^{\lambda x} \nabla^2 - 2h_1 \frac{\partial}{\partial x} \right) v_1 = 0$$

$$\left( e^{\lambda x} \nabla^2 - 2h_1 \frac{\partial}{\partial x} \right) u_1 = 0$$

$$\text{with } \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0 \quad \text{where } 2h_1 = \frac{U\rho_0}{\mu}$$

Since the vortex lines must be circles having the axis of  $x$  as common axis, we may assume

$$\xi = 0, \quad \eta = -\frac{\partial \chi}{\partial x}, \quad \zeta = \frac{\partial \chi}{\partial y} \quad (3.2)$$

where  $\chi$  is a function of  $r$  and  $\omega$  only, where  $\omega$  is the distance from the axis of  $x$

Proceeding as in Case I, we get

$$\left( e^{\lambda x} \nabla^2 - 2h_1 \frac{\partial}{\partial x} \right) \eta = \lambda e^{\lambda x} \nabla^2 w_1 - \frac{\lambda}{\mu} e^{\lambda x} \frac{\partial p}{\partial x}$$

$$\left( e^{\lambda x} \nabla^2 - 2h_1 \frac{\partial}{\partial x} \right) \zeta = -\lambda e^{\lambda x} \nabla^2 v_1 + \frac{\lambda}{\mu} e^{\lambda x} \frac{\partial p}{\partial y}$$

or

$$\left\{ e^{\lambda x} \nabla^2 + \left( \lambda e^{\lambda x} - 2h_1 \right) \frac{\partial}{\partial x} \right\} \eta = -\frac{\lambda}{\mu} e^{\lambda x} \frac{\partial p}{\partial x}$$

$$\left\{ e^{\lambda x} \nabla^2 + \left( \lambda e^{\lambda x} - 2h_1 \right) \frac{\partial}{\partial x} \right\} \zeta = \frac{\lambda}{\mu} e^{\lambda x} \frac{\partial p}{\partial y}$$

so that

$$\left\{ e^{\lambda x} \nabla^2 + \left( \lambda e^{\lambda x} - 2h_1 \right) \frac{\partial}{\partial x} \right\} \chi = \frac{\lambda}{\mu} e^{\lambda x} p \quad (6.2)$$

an additive function of  $x$  only being obviously irrelevant

$$\begin{aligned} 2k_1 \frac{\partial u_2}{\partial x} &= e^{\lambda x} \Delta^2 u_2 + \frac{\lambda}{\mu} e^{\lambda x} p \\ &= -e^{\lambda x} \left( \frac{\partial^2 \chi}{\partial y^2} + \frac{\partial^2 \chi}{\partial z^2} \right) + \frac{\lambda}{\mu} e^{\lambda x} p \\ &= -e^{\lambda x} \frac{\partial^2 \chi}{\partial x^2} + (\lambda e^{\lambda x} - 2k_1) \frac{\partial \chi}{\partial x} \end{aligned}$$

$$2h_1 \frac{\partial v_2}{\partial x} = e^{\lambda x} \nabla^2 v_2 = e^{\lambda x} \frac{\partial^2 \chi}{\partial x \partial y}$$

$$2k_1 \frac{\partial w_2}{\partial x} = e^{\lambda x} \nabla^2 w_2 = e^{\lambda x} \frac{\partial^2 \chi}{\partial x \partial z}$$

whereby

$$\begin{aligned} u_2 &= \frac{1}{2k_1} \left\{ e^{\lambda x} \frac{\partial \chi}{\partial x} - 2k_1 \chi \right\} \\ v_2 &= \frac{1}{2h_1} \left\{ e^{\lambda x} \frac{\partial \chi}{\partial y} - \lambda \int e^{\lambda x} \frac{\partial \chi}{\partial y} dx \right\} \\ w_2 &= \frac{1}{2k_1} \left\{ e^{\lambda x} \frac{\partial \chi}{\partial z} - \lambda \int e^{\lambda x} \frac{\partial \chi}{\partial z} dx \right\} \end{aligned}$$

Now we solve for  $\chi$  given by (6.2)

$$\begin{aligned} e^{\lambda x} \nabla^2 \chi + (\lambda e^{\lambda x} - 2k_1) \frac{\partial \chi}{\partial x} &= \frac{\lambda}{\mu} e^{\lambda x} p = \frac{\rho_0 l}{\mu} \lambda \frac{\partial \Phi}{\partial x} \\ &= 2k_1 \lambda \frac{\partial \Phi}{\partial x} \text{ where } \nabla^2 \Phi = 0 \end{aligned}$$

Following the same argument in Case I and writing  $\Phi = RS$  and  $\chi = \chi^* S$ , where  $\frac{d^2 R}{dx^2} - KR = 0$ ,  $\nabla_1^2 S + KS = 0$  and  $\chi^*$  is a function of  $x$  only, we get the differential equation for  $\chi^*$  to be

$$e^{\lambda x} \left( \frac{d^2 \chi^*}{dx^2} - K \chi^* \right) + (\lambda e^{\lambda x} - 2k_1) \frac{d\chi^*}{dx} = 2k_1 \lambda \frac{dR}{dx}$$

$$\text{or} \quad \frac{d^2 \chi^*}{dx^2} + (\lambda - 2k_1 e^{-\lambda x}) \frac{d\chi^*}{dx} - K \chi^* = 2k_1 \lambda e^{-\lambda x} \frac{dR}{dx}$$

$$\text{Put} \quad e^{-\lambda x} = x_1, \quad \text{i.e., } \lambda x = \log \frac{1}{x_1}$$

$$\text{or} \quad \frac{dx_1}{dz} = -\lambda e^{-\lambda x} = -\lambda x_1$$

$$\begin{aligned}\frac{d\lambda^*}{dx} &= \frac{d\lambda^*}{dx_1} \frac{dx_1}{dx} = -\lambda x_1 \frac{d\lambda^0}{dx_1} \\ \frac{d^2\lambda^*}{dx^2} &= \frac{d}{dx_1} \left( -\lambda x_1 \frac{d\lambda^*}{dx_1} \right) \frac{dx_1}{dx} = \lambda^2 x_1 \frac{d}{dx_1} \left( x_1 \frac{d\lambda^*}{dx_1} \right) \\ &= \lambda^2 \left( x_1 \frac{d^2\lambda^*}{dx_1^2} + x_1 \frac{d\lambda^0}{dx_1} \right)\end{aligned}$$

Substituting, we get

$$\lambda^2 \left( x_1 \frac{d^2\lambda^*}{dx_1^2} + x_1 \frac{d\lambda^0}{dx_1} \right) + (\lambda - 2k_1 x_1)(-\lambda x_1) \frac{d\lambda^0}{dx_1} - \lambda \lambda^0 = 2k_1 \lambda x_1 \frac{dR}{dx_1} (-\lambda x_1)$$

$$\text{or} \quad \lambda^2 x_1 \frac{d^2\lambda^*}{dx_1^2} + 2k_1 \lambda x_1 \frac{d\lambda^*}{dx_1} - \lambda \lambda^* = -2k_1 \lambda^2 x_1 \frac{dR}{dx_1} \quad (b \ 21)$$

Let us first find the complementary function given by

$$D\lambda^* \equiv \lambda^2 x_1 \frac{d^2\lambda^*}{dx_1^2} + 2k_1 \lambda x_1 \frac{d\lambda^*}{dx_1} - \lambda \lambda^* = 0$$

Constructing an expression

$$\bar{V} = c_0 x_1^a + c_1 x_1^{a+1} + c_2 x_1^{a+2} + \dots + c_n x_1^{a+n} + \dots$$

we have

$$D\bar{V} = c_0 \{ \lambda^2 a(a-1) - \lambda \} x_1^a$$

provided  $2k_1 \lambda c_{n-1} (a + n - 1) = \{ \lambda^2 (a+n)(a+n-1) - k \} c_n$ , for  $n \geq 1$

So the indicial equation is given by

$$\lambda^2 a(a-1) - k = 0$$

$$\text{and } \frac{c_n x_1}{c_{n-1}} = \frac{2k_1 \lambda (a+n-1)}{\lambda^2 (a+n)(a+n-1) - k} x_1$$

$$\longrightarrow 0 \quad \text{as } n \longrightarrow \infty$$

Hence, the series thus obtained is absolutely and uniformly Convergent for all values of  $x_1$

Now

$$\lambda^2 \alpha^2 - \lambda^2 \alpha - k = 0$$

$$\alpha = \frac{\lambda^2 \pm \sqrt{\lambda^4 + 4k}}{2\lambda^2} = \frac{\lambda \pm \sqrt{\lambda^2 + 4k}}{2\lambda}$$

If the roots  $\alpha_1$  and  $\alpha_2$  do not differ by an integer we shall get the two solutions as

$$\chi_1^* = [\bar{V}]_{\alpha=\alpha_1} \quad \text{and} \quad \chi_2^* = [\bar{V}]_{\alpha=\alpha_2}$$

Now

$$c_n = \frac{2k_1 \lambda (a+n-1)}{\lambda^2 (a+n)(a+n-1) - k} c_{n-1}, \quad \text{for } n \geq 1$$

$$c_1 = \frac{2k_1 \lambda a}{\lambda^2 (a+1)a - k} c_0$$

$$c_2 = \frac{2k_1\lambda(a+1)}{\lambda^2(a+2)(a+1)-k} c_1 = \frac{2k_1\lambda(a+1)}{\lambda^2(a+2)(a+1)-k} \frac{2k_1\lambda a}{\lambda^2(a+1)a-k} c_0$$

$$c_3 = \frac{2k_1\lambda(a+1)}{\lambda^2(a+3)(a+2)-k} \frac{2k_1\lambda(a+1)}{\lambda^2(a+2)(a+1)-k} \frac{2k_1\lambda a}{\lambda^2(a+1)a-k} c_0 \text{ etc}$$

Hence

$$V = c_0 x_1^a \left( 1 + \frac{2k_1\lambda a}{\lambda(a+1)a-k} x_1 + \frac{2k_1\lambda(a+1)}{\lambda^2(a+2)(a+1)-k} \frac{2k_1\lambda a}{\lambda^2(a+1)a-k} x_1^2 \right. \\ \left. + \frac{2k_1\lambda(a+1)}{\lambda^2(a+3)(a+2)-k} \frac{2k_1\lambda(a+1)}{\lambda^2(a+2)(a+1)-k} \frac{2k_1\lambda a}{\lambda^2(a+1)a-k} x_1^3 + \dots \right)$$

Hence the complete solution is given by

$$X = S(BX_1^* + \lambda X_2)^0 \text{ where } S = \lambda_0 J_0(\beta_1 \omega) \text{ if } \beta_1^2 = / \\ - B_0 I_0(\beta_2 \omega) \text{ if } \beta_2^2 = -/$$

and

$$\left. \begin{aligned} A &= F - \gamma_1 \int \frac{dR}{dx_1} \chi_1 e^{\int \frac{2k_1}{\lambda} dx} dx_1 \\ B &= F + 2k_1 \int \frac{dR}{dx_1} \chi_2 e^{\int \frac{2k_1}{\lambda} dx} dx_1 \end{aligned} \right\} \begin{aligned} &F \text{ and } F \text{ being arbitrary} \\ &\text{constants} \end{aligned}$$

which are integrable

Now

$$R = c_1 e^{\sqrt{k} x} + c_2 e^{-\sqrt{k} x}$$

$$= c_1 e^{\frac{\sqrt{k}}{\lambda} \log \frac{1}{x_1}} + c_2 e^{-\frac{\sqrt{k}}{\lambda} \log \frac{1}{x_1}}$$

$$= c'_1 (x_1)^{\frac{\sqrt{k}}{\lambda}} + c'_2 (x_1)^{-\frac{\sqrt{k}}{\lambda}}$$

Hence a complete solution of (A<sub>4</sub>) is found

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# THE ARMS OF A SPIRAL NEBULA IN RESISTING MEDIUM I

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In this paper we have investigated the actual path of an ejected material from the equatorial plane taking account of resistance. The space outside a nebula is not totally devoid of matter, and thus the ejected particle would travel in resisting medium. Moreover Eddington's<sup>4</sup> theoretical researches as well as Plaskett<sup>5</sup> and Pearce's observational investigations show that interstellar space (within the confines of the galaxy) is not empty but is fitted with a very rarefied gas of "Substantially uniform density."

We have assumed Banerji's<sup>1</sup> configuration of a rotating gaseous mass of uniform density which surrounds spheroidal homogeneous mass of incompressible material. The total intensity of attraction  $f^{(n)}$  at an external point in the equatorial plane is assumed to be made up of two parts—one part is due to the attraction of the larger spheroid of equatorial radius  $a$  and density  $\rho_1$  and the other is due to the smaller spheroid of equatorial radius  $K_0 a$  and density  $(\rho_0 - \rho_1)$ .

Now,

$$f = 2\pi(1-e^2)^{\frac{1}{2}} \left[ \frac{1}{2} \frac{a^2}{r^2} \{K_0^2 \rho_0 + \rho_1(1-K_0^2)\} + \frac{1}{2} \frac{a^2 e^2}{r^2} \{K_0^2 \rho_0 + \rho_1(1-K_0^2)\} + \right. \\ \left. + \frac{1}{2} \frac{3}{4} \frac{2n-1}{2n} \frac{2}{2n+3} \frac{a^{2n+3} e^{2n}}{r^{2n+2}} \left\{ K_0^{2n+3} \rho_0 + \rho_1(1-K_0^{2n+3}) \right\} \right]$$

By keeping only upto  $e^{2n}$

Hence we have

$$f = \frac{A_0}{r^2} + \frac{A_1}{r^4} + \frac{A_n}{r^{2n+2}}$$

where

$$A_0 = 2\pi a^2(1-e^2)^{\frac{1}{2}} \rho_0 \left\{ K_0^2 + \frac{\rho_1}{\rho_0}(1-K_0^2) \right\} = 2\pi a^2 \rho_0(1-e^2)^{\frac{1}{2}} \alpha_0$$

$$A_1 = 2\pi a^2(1-e^2)^{\frac{1}{2}} \rho_0 \frac{1}{2} a^2 e^2 \left\{ K_0^2 + \frac{\rho_1}{\rho_0}(1-K_0^2) \right\} = 2\pi a^2 \rho_0(1-e^2)^{\frac{1}{2}} a^2 e^2 \alpha_1$$

• • •

$$A_n = 2\pi a^2(1-e^2)^{\frac{1}{2}} \rho_0 a^{2n} e^{2n} \frac{1}{2} \frac{3}{4} \frac{2n-1}{2n} \left\{ K_0^{2n+3} + \frac{\rho_1}{\rho_0}(1-K_0^{2n+3}) \right\} \cdot \frac{2}{2n+3} \\ = 2\pi a^2(1-e^2)^{\frac{1}{2}} \rho_0 a^{2n} e^{2n} \alpha_n$$



where

$$\alpha_0 = \frac{1}{2} \left\{ K_0^2 + \frac{\rho_1}{\rho_0} (1 - K_0^2) \right\}$$

$$\alpha_1 = \frac{1}{2} \left\{ K_0^2 + \frac{\rho_1}{\rho_0} (1 - K_0^2) \right\}$$

$$\alpha_n = \frac{1}{2} \frac{(2n-1)}{2n} \frac{2}{2n+3} \left\{ K_0^{2n+3} + \frac{\rho_1}{\rho_0} (1 - K_0^{2n+3}) \right\}$$

(a) Resistance<sup>6</sup> varies as  $\frac{v}{r^3}$ , where  $v$  is the velocity and  $r$ , distance from the centre

The radial and transverse components are  $-\frac{L}{r^3} \frac{dr}{dt}$  and  $-\frac{L}{r^3} r\theta$  where  $L$  is constant and small,

Equations of motion now become

$$\ddot{r} - r\dot{\theta}^2 = -f - \frac{L}{r^3} \frac{dr}{dt} \quad (1)$$

$$\frac{1}{r} \frac{d}{dt} (r^2 \dot{\theta}) = -\frac{L}{r^3} r\theta \quad (2)$$

$$\text{Put } r = \frac{1}{u}$$

$$r = -\frac{1}{u^3} \frac{du}{dt}$$

$$\frac{d}{dt} \left( u^{-4} \frac{du}{dt} \right) + 2u^{-5} \dot{u}^2 + u^{-3} \theta^2 = (A_0 + A_1 u^2 + A_2 u^{2n}) - L u^{-2} u \quad (3)$$

Equation (2) becomes

$$\frac{d}{dt} (u^{-2} \theta) = -L \theta$$

$$u^{-2} \theta = h_0 - L\theta = H$$

or

$$\frac{d}{dt} = H u^2 \frac{d}{d\theta}$$

here  $h_0$  is constant, when  $\theta=0$ ,  $u=u_0$ , we have  $h_0 = a^2 \omega$  where  $\omega$  is the initial angular velocity.

Now equation (3) becomes

$$\frac{d^2 u}{d\theta^2} + u = \frac{1}{h_0^2} \left( A_0 + A_1 u^2 + A_2 u^{2n} \right) \left( 1 + 2 \frac{L\theta}{h_0} \right)$$

where higher powers of  $L$  are neglected

$$\text{Now put } 2 \frac{2\pi \rho_0 \alpha_0}{\omega^2} = m$$

By putting the values of  $\Pi$ ,  $\rho_0$ ,  $\alpha_0$  and  $\omega^2$ , we see that  $m$  is less than 1.  
i.e.,  $m$  is  $\ll 1$ , small and less than 1

$$m < 1$$

$$\frac{d^2 u}{d\theta^2} + u = \frac{mu_0}{2} \left[ 1 + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} u^2 - \frac{e^2}{2} \right] \left[ 1 + \frac{2L\theta}{h_0} \right]$$

keeping terms up to  $e^2$

To the first approximation we can take the value of  $\theta^{(0)}$

$$\theta = \left( 1 + \frac{\alpha_1 m^2 e^2}{4 \alpha_0} \right) \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \\ - e^2 mu_0 \left\{ \frac{\alpha_1}{6\alpha_0 u_0^2} \sqrt{(u_0 - u)[u + u_0(1-m)]} + \frac{B}{u_0} \sqrt{\frac{u_0 - u}{u + u_0(1-m)}} \right\}$$

Thus we have

$$\begin{aligned} \frac{d^2 u}{d\theta^2} + u &= \frac{mu_0}{2} \left[ 1 + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} u^2 - \frac{e^2}{2} \right] \\ &+ \frac{Lm u_0}{h_0} \left[ \left( 1 + \frac{\alpha_1 m^2 e^2}{4 \alpha_0} - \frac{e^2}{2} \right) \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right. \\ &+ \frac{\alpha_1 e^2}{\alpha_0 u_0^2} u^2 \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \\ &\left. - e^2 mu_0 \left\{ \frac{\alpha_1}{6\alpha_0 u_0^2} \sqrt{(u_0 - u)[u + u_0(1-m)]} + \frac{B}{u_0} \sqrt{\frac{u_0 - u}{u + u_0(1-m)}} \right\} \right] \\ \left( \frac{du}{d\theta} \right)^2 + u^2 &= mu_0 \left[ u + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \frac{u^3}{3} - \frac{e^2 u}{2} \right] + \frac{2Lmu_0}{h_0} \left[ \left( 1 + \frac{\alpha_1 m^2 e^2}{4 \alpha_0} - \frac{e^2}{2} \right) \right. \\ &\left\{ u \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) + \frac{1}{2} \left[ (2-m)^2 u_0^2 - (2u - mu_0)^2 \right]^{\frac{1}{2}} \right. \\ &- \frac{mu_0}{2} \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \left. \right\} + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \left\{ \frac{u^3}{3} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right. \\ &+ \frac{1}{2} \left[ \frac{u^2}{12} + \frac{5}{48} mu_0 u + \frac{u_0^2}{96} (16 - 16m + 15m^2) \right] \left[ (2-m)^2 u_0^2 - (2u - mu_0)^2 \right]^{\frac{1}{2}} \\ &- \frac{1}{2} \frac{mu_0^2}{8} (3 - 3m + \frac{1}{2} m^2) \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \left. \right\} \\ &- e^2 mu_0 \left\{ \frac{\alpha_1}{6\alpha_0 u_0^2} \left[ \left( \frac{u}{2} - \frac{mu_0}{4} \right) \sqrt{u_0 - u} [u + u_0(1-m)] \right] \right. \end{aligned}$$

$$+ \frac{(2-m)^2}{8} u_0^2 \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \Big] + \frac{B}{u_0} \left[ \sqrt{(u_0 - u)(u + u_0(1-m))} \right. \\ \left. + \frac{(2-m)}{2} u_0 \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \right] \Big\} + E$$

where E is the constant of integration, which can be found out by putting the initial conditions,  $u = u_0$  and  $\frac{du}{d\theta} = 0$

Here we introduce new constants

$$B = \left[ \frac{\alpha_1}{3\alpha_0} (1 + m^2 - m) - \frac{1}{2} \right] \frac{1}{(2-m)}$$

$$B_1 = \frac{16 - 16m + 15m^2}{96} \text{ and } B_2 = \frac{m}{32} (12 - 12m + 5m^2)$$

Hence we have

$$\left( \frac{du}{d\theta} \right)^2 = mu_0 \left[ (u - u_0) + \frac{\alpha_1 e^2}{3\alpha_0 u_0^2} (u^2 - u_0^2) - \frac{e^2}{2} (u - u_0) \right] \\ + \frac{2Lmu_0}{h_0} \left[ \left( 1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2} \right) \left\{ \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \left( u - \frac{mu_0}{2} \right) \right. \right. \\ \left. \left. + \frac{1}{2} \left[ (2-m)^2 u_0^2 - (2u - mu_0)^2 \right]^{\frac{1}{2}} \right\} + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \left\{ \frac{u^2}{3} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right. \right. \right. \\ \left. \left. + \frac{1}{2} \left( \frac{u^2}{12} + \frac{5}{48} mu_0 u + B_1 u_0^2 \right) \left[ (2-m)^2 u_0^2 - (2u - mu_0)^2 \right]^{\frac{1}{2}} \right. \right. \right. \\ \left. \left. - \frac{1}{2} B_2 u_0^2 \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right\} \right. \\ \left. - e^2 mu_0 \left\{ \frac{\alpha_1}{6\alpha_0 u_0^2} \left[ \left( \frac{u}{2} - \frac{mu_0}{4} \right) \sqrt{(u_0 - u)(u + u_0(1-m))} \right. \right. \right. \right. \\ \left. \left. + \frac{(2-m)^2}{8} u_0^2 \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right] + \frac{B}{u_0} \left[ \sqrt{(u_0 - u)(u + u_0(1-m))} \right. \right. \right. \\ \left. \left. + \frac{(2-m)u_0}{2} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right) \right] \right\} \right] + u_0^2 - u^2 \\ \frac{du}{d\theta} = \sqrt{(u_0 - u)(u + u_0(1-m))} \left[ 1 + mu_0 \frac{\left\{ \frac{e^2}{2} - \frac{\alpha_1 e^2}{3\alpha_0 u_0^2} (u^2 + mu_0 u + u_0^2) \right\}}{u + u_0(1-m)} \right. \\ \left. + \frac{2Lmu_0}{h_0} \left\{ \left( 1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2} \right) \frac{\left( u - \frac{mu_0}{2} \right) \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\Pi}{2} \right)}{(u_0 - u)(u + u_0(1-m))} \right. \right. \right.$$

$$\begin{aligned}
& + \frac{\left(1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2}\right)}{\sqrt{(u_0 - u)[u + u_0(1 - m)]}} + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \left[ \frac{\frac{u^2}{3} \left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{(u_0 - u)[u + u_0(1 - m)]} \right. \\
& + \frac{4}{3} \frac{\frac{u^2}{12} + \frac{5}{48} mu_0 u + B_1 u_0^2}{\sqrt{(u_0 - u)[u + u_0(1 - m)]}} - \frac{1}{2} B_2 u_0^2 \left. \frac{\left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{(u_0 - u)[u + u_0(1 - m)]} \right] \\
& - e^2 m u_0 \left[ \frac{\alpha_1}{6\alpha_0 u_0^2} \frac{\left( \frac{u}{2} - \frac{mu_0}{4} \right)}{\sqrt{(u_0 - u)[u + u_0(1 - m)]}} \right. \\
& \quad + \frac{\alpha_1}{6\alpha_0 u_0^2} \frac{(2 - m)^2 u_0^2}{8} \frac{\left( \sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{(u_0 - u)[u + u_0(1 - m)]} \\
& + \frac{B}{u_0} \frac{1}{\sqrt{(u_0 - u)[u + u_0(1 - m)]}} + \frac{B}{u_0} \frac{(2 - m)u_0}{2} \\
& \quad \left. \frac{\left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{(u_0 - u)[u + u_0(1 - m)]} \right] \Bigg\} \Bigg]^{1/2} \\
\theta + \epsilon = & \int \frac{du}{\sqrt{(u_0 - u)[u + u_0(1 - m)]}} + \frac{mu_0 e^2}{2} \int \frac{\left[ \frac{\alpha_1}{3\alpha_0 u_0^2} \left( u^2 + uu_0 + u_0^2 \right) - \frac{1}{2} \right]}{(u_0 - u)^{1/2} [u + u_0(1 - m)]^{3/2}} du \\
& - \frac{1}{h_0} \frac{mu_0}{\left[ \left( 1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2} \right) \right]} \int \frac{\left( u - \frac{mu_0}{2} \right) \left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{\{(u_0 - u)[u + u_0(1 - m)]\}^{3/2}} du \\
& + \left( 1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2} \right) \int \frac{du}{(u_0 - u)[u + u_0(1 - m)]} + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \\
& \quad \cdot \left\{ \int \frac{\frac{u^2}{3} \left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right)}{\{(u_0 - u)[u + u_0(1 - m)]\}^{3/2}} du \right. \\
& + \frac{4}{3} \int \frac{\left( \frac{u^2}{12} + \frac{5}{48} mu_0 u + B_1 u_0^2 \right) du}{(u_0 - u)[u + u_0(1 - m)]} - \frac{1}{2} B_2 u_0^2 \int \frac{\left( \frac{\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\Pi}{2} \right) du}{\{(u_0 - u)[u + u_0(1 - m)]\}^{3/2}} \Bigg\}
\end{aligned}$$

$$\begin{aligned}
& -e^{\frac{1}{2}mu_0} \left\{ \frac{\alpha_1}{6\alpha_0 u_0^{\frac{1}{2}}} \int \frac{\left(u - \frac{mu_0}{2}\right) du}{2(u_0 - u)[u + u_0(1-m)]} + \frac{\alpha_1}{6\alpha_0 u_0^{\frac{1}{2}}} \right. \\
& \quad \left. \frac{(2-m)^2 u_0^{\frac{1}{2}}}{8} \int \frac{\left(\sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2}\right)}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1-m)]^{\frac{1}{2}}} \right. \\
& \quad \left. + \frac{B}{u_0} \int \frac{du}{(u_0 - u)[u + u_0(1-m)]} + \frac{B}{u_0} \frac{(2-m)u_0}{2} \int \frac{\left(\sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2}\right) du}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1-m)]^{\frac{1}{2}}} \right\}
\end{aligned}$$

Hence we get

$$\begin{aligned}
\theta + c = & \left(1 + \frac{m^2 e^2 \alpha_1}{4\alpha_0}\right) \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - e^{\frac{1}{2}mu_0} \left\{ \frac{\alpha_1}{6\alpha_0 u_0^{\frac{1}{2}}} \sqrt{(u_0 - u)[u + u_0(1-m)]} \right. \\
& + \frac{B}{u_0} \sqrt{\frac{u_0 - u}{u + u_0(1-m)}} \left. \right\} - \frac{Lmu_0}{h_0} \left[ \left(1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2}\right) \left\{ \frac{\sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2}}{\sqrt{(u_0 - u)[u + u_0(1-m)]}} \right. \right. \\
& \left. \left. - \frac{1}{(2-m)u_0} \log \frac{u + u_0(1-m)}{u_0 - u} \right\} + \left(1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2}\right) \frac{1}{(2-m)u_0} \log \frac{u + u_0(1-m)}{u_0 - u} \right. \\
& + \frac{\alpha_1 e^2}{6\alpha_0 u_0^{\frac{1}{2}}} \left\{ \left[ (2-m)u_0 \left\{ \left[ \frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0} \right]^{\frac{1}{2}} + \frac{(2-m)u_0}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right\} \right. \right. \\
& + 3mu_0 \left[ \frac{(2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} - \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \right] \\
& + \left. \left[ \frac{3m^2 u_0^2}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} + \frac{u_0 m^2}{(2-m)^2} \frac{(2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right] \right\} \times \\
& \left[ \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right] - \left[ (2-m)u_0 \left\{ \frac{2u - mu_0}{(2-m)u_0} + \frac{1}{2} \log \frac{u + u_0(1-m)}{u_0 - u} \right\} \right. \\
& \left. - 3mu_0 \left\{ \log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}} + \frac{1}{2} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \right)^2 \right\} \right. \\
& + \left. \frac{3m^2 u_0}{2(2-m)} \log \frac{u + u_0(1-m)}{u_0 - u} - \frac{u_0 m^2}{(2-m)^2} \log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}} \right\} \\
& + \frac{\alpha_1 e^2}{\alpha_0 u_0^{\frac{1}{2}}} \left\{ -\frac{u}{9} + \frac{u_0}{(2-m)} \left[ \left(1 - m + \frac{m^2}{2}\right)^{\frac{1}{2}} + \frac{1}{2} m^2 + \frac{1}{2} B_1 \right] \log \frac{u + u_0(1-m)}{u_0 - u} \right. \\
& \left. - \frac{mu_0}{2} \left( \frac{1}{3} + \frac{1}{2} \right) \log (u_0 - u)[u + u_0(1-m)] \right\}
\end{aligned}$$

$$\begin{aligned}
& -\frac{3}{2-m} \frac{B_1 u_0}{2-m} \left\{ \sin^{-1} \left( \frac{2u - mu_0 - \frac{\pi}{2}}{2 - m u_0} \right) (2u - mu_0) \right. \\
& \quad \left. + \log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}} \right\} \\
& \quad - e^2 mu_0 \left\{ -\frac{a_1}{2\alpha_0 u_0} \log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}} \right. \\
& \quad \left. + \frac{a_1}{1-\alpha_0 u_0} \left[ \frac{\left( \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{2 - m u_0} \right) (2u - mu_0)}{\sqrt{(2-m)^2 u_0^2 - (2u - mu_0)^2}} + \log \sqrt{\frac{(2-m)^2 u_0^2 - 2u - mu_0}{(2-m)u_0}} \right] \right. \\
& \quad \left. + \frac{B}{u_0^2 (2-m)} \log \frac{u + u_0(1-m)}{u_0 - u} + \frac{2B}{u_0^2 (2-m)} \left[ \left( \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{2 - m u_0} \right) (2u - mu_0) \right. \right. \\
& \quad \left. \left. + \log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}} \right] \right\}
\end{aligned}$$

We substitute  $\frac{1}{2} \log u_0 - u + \frac{1}{2} \log [u + u_0(1-m)] - \log \frac{(2-m)u_0}{2}$  for  $\log \sqrt{\frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0}}$  and find that sum of the coefficients of all the terms which become infinite on putting initial conditions, vanish

Hence we have

$$\begin{aligned}
\theta = & \left( \frac{1 + m^2 e^2 a_1}{4\alpha_0} \right) \left( \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{2 - m u_0} \right) - e^2 mu_0 \left\{ \frac{a_1 \sqrt{(u_0 - u)} [u + u_0(1-m)]}{6\alpha_0 u_0^2} \right. \\
& \left. + \frac{\beta}{u_0} \sqrt{\frac{u_0 - u}{u + u_0(1-m)}} \right\} - \frac{Lmu_0}{h_0} \left[ \left( \frac{1 + \alpha_1 m^2 e^2 - e^2}{4\alpha_0} - \frac{e^2}{2} \right) \frac{\left( \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{2 - m u_0} \right)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right. \\
& \left. + \frac{\alpha_1 e^2}{6\alpha_0 u_0^2} \left\{ \left[ u_0(2-m) \right] \left\{ \frac{(2-m)^2 u_0^2 - (2u - mu_0)^2}{(2-m)u_0} \right\}^{\frac{1}{2}} + \frac{(2-m)u_0}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right\} \right. \\
& \left. + 3mu_0 \left\{ \frac{2u}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \right\} \right. \\
& \left. + \frac{m^2 u_0}{(2-m)^2} \left\{ \frac{(2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right\} \left[ \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{(2-m)u_0} - \frac{\pi}{2} \right] \right. \\
& \left. - \left[ 2(u - u_0) - \frac{1}{2} mu_0 \left\{ \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} \right)^2 - \left( \frac{\pi}{2} \right)^2 \right\} \right] \right. \\
& \left. + \frac{\alpha_1 e^2}{\alpha_0 u_0^2} \left\{ \frac{(u_0 - u)}{9} - \frac{\beta}{(2-m)^2} \left[ \frac{\left( \sin^{-1} \frac{2u - mu_0 - \frac{\pi}{2}}{(2-m)u_0} \right) (2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right] \right\} \right.
\end{aligned}$$

$$-e^2 m u_0 \left\{ \frac{\alpha_1}{12\alpha_0 u_0} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) \frac{(2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} + \right. \\ \left. \frac{2B}{(2-m)u_0} \left[ \log \frac{u + u_0(1-m)}{(2-m)u_0} + \frac{\left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) (2u - mu_0)}{[(2-m)^2 u_0^2 - (2u - mu_0)^2]^{\frac{1}{2}}} \right] \right\}$$

With a little simplification we get

$$\theta = \left( \frac{1 + m^2 e^2 \alpha_1}{4\alpha_0} \right) \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) - e^2 m u_0 \left\{ \frac{\alpha_1}{6\alpha_0 u_0} \sqrt{(u_0 - u)(u + u_0(1-m))} \right. \\ \left. + \frac{B}{u_0} \sqrt{\frac{u_0 - u}{u + u_0(1-m)}} \right\} - \frac{L m u_0}{h_0} \left\{ \frac{c_1}{u_0} (2u - mu_0) + c_2 \right\} \times \\ \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) + \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) \frac{\alpha_1 e^2}{6\alpha_0 u_0} \sqrt{(u_0 - u)(u + u_0(1-m))} \\ - \frac{2B e^2 m}{u_0(2-m)} \log \frac{u + u_0(1-m)}{(2-m)u_0} + \frac{4}{9} \frac{\alpha_1 e^2}{\alpha_0 u_0^2} (u_0 - u) \\ - \frac{\alpha_1 e^2 m}{4\alpha_0 u_0} \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right)^2$$

$$\text{where } c_1 = \frac{\alpha_1 e^2}{\alpha_0} \left[ \frac{m}{4} + \frac{m^2}{12(2-m)^2} - \frac{4}{3} \frac{B}{(2-m)^2} - \frac{m}{24} \right] - \frac{e^2 m B}{(2-m)}$$

$$\text{and } c_2 = \frac{\alpha_1 e^2}{3\alpha_0} \left( 1 - m + m^2 \right) + \frac{1}{2} \left( 1 + \frac{\alpha_1 m^2 e^2}{4\alpha_0} - \frac{e^2}{2} \right)$$

In order to see the curve at a sufficiently great distance we expand the above in powers of  $\frac{u}{u_0}$ , keeping only upto  $\frac{u}{u_0}$  and neglecting its 2nd and higher powers and further we neglect 3rd and higher powers of  $\frac{m}{2-m}$ , since  $m$  is small

$$\theta = \frac{u}{u_0} \left[ \frac{2}{2-m} \left( \frac{1 + m^2 e^2 \alpha_1}{4\alpha_0} \right) - \frac{e^2 \alpha_1 m^2}{12\alpha_0 (1-m)^2} + \frac{e^2 m B (2-m)}{2(1-m)^2} \right. \\ \left. - \frac{L m}{h_0} \left\{ \frac{1}{\sqrt{1-m}} \left[ \frac{2(c_1 - c_2 m)}{(2-m)} - \left( \frac{m}{2-m} + \frac{\pi}{2} \right) \left[ \frac{(2-m)^2 c_1 - m c_2}{2(1-m)} \right] \right. \right. \right. \\ \left. \left. + \frac{\alpha_1 e^2}{3\alpha_0} (1-m)^2 \left\{ \frac{2}{2-m} - \left( \frac{\pi}{2} + \frac{m}{2-m} \right) \frac{m}{2(1-m)} \right\} - \frac{2B e^2 m}{(2-m)(1-m)} - \frac{4}{9} \frac{\alpha_1 e^2}{\alpha_0} \right. \right. \right. \\ \left. \left. \left. + \frac{\alpha_1 e^2 m \pi}{2\alpha_0 (2-m)} \right] \right\} - \left( \frac{m}{2-m} + \frac{\pi}{2} \right) \left( 1 + \frac{m^2 e^2 \alpha_1}{4\alpha_0} \right) - \frac{m e^2 \alpha_1 (1-m)^{\frac{1}{2}}}{6\alpha_0} \right]$$

$$\begin{aligned}
& -\frac{e^2 m B}{(1-m)^{\frac{1}{2}}} + \frac{Lm}{h_0} \left\{ \left( \frac{c_1 - c_1 m}{(1-m)^{\frac{1}{2}}} \right) \left( \frac{m}{2-m} + \frac{\Pi}{2} \right) \right. \\
& + \left( \frac{\Pi}{2} + \frac{m}{2-m} \right) \left( \frac{\alpha_1 e^2 (1-m)^{\frac{1}{2}}}{3\alpha_0} + \frac{2Be^2 m}{(2-m)} \log \frac{1-m}{2-m} - \frac{4}{9} \frac{e^2 \alpha_1}{\alpha_0} \right. \\
& \left. \left. + \frac{\alpha_1 e^2 m}{4\alpha_0} \left( \frac{m}{2-m} + \frac{\Pi}{2} \right) \right) \Pi \right\}
\end{aligned}$$

which can be put in the form of

$$\theta = (k_1 - k_2 u_0^2) \frac{u}{u_0} - k_3 + k_4 u_0^2 \quad (4)$$

where  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are all constants and  $u_0 = \frac{1}{a}$  (constant)

Thus the curve given by equation (4) is a deformed spiral

In the end I wish to record my respectful thanks to Prof A C Banerji, for his keen interest in my work

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## ON THE THEORY OF A SPIRAL NEBULA II

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In this paper we have assumed Banerji's<sup>1</sup> configuration of a rotating gaseous mass of uniform density which surrounds a spheroidal homogeneous mass of incompressible material. The size of the central mass is assumed to be small compared to that of the outer boundary of the gaseous structure. We have investigated the actual path of an ejected material from the equatorial plane. In a recent paper,<sup>2</sup> I have worked out a case of a rotating spheroidal central mass of a small but finite dimensions and uniform density surrounded by a spheroidal structure of rotating compressible gas of variable density.

Lindblad<sup>3</sup> has considered the case of a condensed point nucleus which is surrounded by a spheroidal galaxy of stars of uniform density from which arms emanate. Now recent investigations by Plaskett<sup>4</sup> and Pearce about our galactic system show that "the whole galactic system is immersed in a gaseous substratum consisting of atoms of various elements . . . the separate atoms while obeying ordinary gas laws participate in a rotational movement around a distant central mass in galactic longitude  $825^{\circ}$ " so for a mathematical investigation it seems proper to assume that the central core is surrounded by a gaseous mass instead of a galaxy of stars, as assumed by Lindblad. Moreover Eddington's<sup>5</sup> theoretical researches as well as Plaskett<sup>4</sup> and Pearce's observational investigations show that interstellar space (within the confines of the galaxy) is not empty but is filled with a very highly rarefied gas of "substantially uniform density". Smart<sup>6</sup> remarks "The observed feature of galactic rotation may be ascribed to a highly concentrated central mass together with a uniform spheroidal distribution of matter". For mathematical analysis we have assumed a configuration in which there is a central rotating spheroidal core of homogeneous and incompressible material whose density is  $\rho_0$  and which is of small but finite dimensions. This core is again surrounded by a rotating gaseous configuration of mean density  $\rho_1$  which differs slightly from the actual density at any point of the gaseous mass, where  $\rho_0 \gg \rho_1$ .

The total intensity of attraction  $f^2$  at the external point in the equatorial plane is assumed to be made up of two parts, viz., one part is due to the attraction of the

larger spheroid of equatorial radius  $\alpha$  and density  $\rho_1$  and the other is due to the smaller spheroid of equatorial radius  $k_0 \alpha$  and density  $(\rho_0 - \rho_1)$

Now

$$f = 2\pi(1-e^2)^{\frac{1}{2}} \left[ \frac{3}{2} \frac{\alpha^4}{\gamma^2} \{k_0^3 \rho_0 + \rho_1(1-k_0^3)\} + \frac{\alpha^2 e^2}{\gamma^4} \{k_0^3 \rho_0 + \rho_1(1-k_0^3)\} \right. \\ \left. + \frac{1}{2} \frac{8}{4} \frac{(2n-1)}{2n} \frac{2}{2n+3} \frac{\alpha^{2n+2} e^{2n}}{\gamma^{2n+2}} \{k_0^{2n+3} \rho_0 + \rho_1(1-k_0^{2n+3})\} \right]$$

By keeping only up to  $e^{2n}$ ,

$$f = \frac{A_0}{\gamma^2} + \frac{A_1}{\gamma^4} + \dots + \frac{A_n}{\gamma^{2n+2}}$$

where  $A_0 = 2\pi\alpha^4(1-e^2)^{\frac{1}{2}} \rho_0 \frac{3}{2} \{k_0^3 + \frac{\rho_1}{\rho_0}(1-k_0^3)\} = 2\pi\alpha^4 \rho_0(1-e^2)^{\frac{1}{2}} \alpha_0$

$$A_1 = 2\pi\alpha^2(1-e^2)^{\frac{1}{2}} \rho_0 \alpha^2 e^2 \frac{1}{2} \{k_0^3 + \frac{\rho_1}{\rho_0}(1-k_0^3)\} = 2\pi\alpha^2 \rho_0(1-e^2)^{\frac{1}{2}} \alpha^2 e^2 \alpha_1$$

$$A_n = 2\pi\alpha^2(1-e^2)^{\frac{1}{2}} \rho_0 \frac{1}{2} \frac{8}{4} \frac{2n-1}{2n} \frac{2}{2n+3} \alpha^{2n} e^{2n} \{k_0^{2n+3} + \frac{\rho_1}{\rho_0}(1-k_0^{2n+3})\} \\ = 2\pi\alpha^2(1-e^2)^{\frac{1}{2}} \rho_0 \alpha^{2n} e^{2n} \alpha_n$$

where

$$\alpha_0 = \frac{3}{2} \{k_0^3 + \frac{\rho_1}{\rho_0}(1-k_0^3)\}$$

$$\alpha_1 = \frac{1}{2} \{k_0^3 + \frac{\rho_1}{\rho_0}(1-k_0^3)\}$$

$$\alpha_n = \frac{1}{2} \frac{8}{4} \frac{2n-1}{2n} \frac{2}{2n+3} \{k_0^{2n+3} + \frac{\rho_1}{\rho_0}(1-k_0^{2n+3})\}$$

In addition to the force of attraction  $f$  there is also a repulsive force proportional to the distance from the centre of the core which follows from the general theory of relativity. Thus the repulsive force is  $\mu^2 r$  where  $\mu^2$  is very small.

The equation of the orbit of an external particle which has just been ejected in the equatorial plane is

$$\frac{d^2 u}{d\theta^2} + u = \frac{f}{h^2 u^2} - \frac{\mu^2}{h^2 u} = \frac{1}{h^2} [A_0 + A_1 u^2 + \dots + A_n u^{2n}] - \frac{\mu^2}{h^2 u}$$

where  $u = \frac{1}{r}$  and  $\mu^2$  is very small

The effect of some such disturbing factor as tidal action will be to cause a slight perturbation but this leaves  $h$  unchanged, i.e.,  $h = a^2 \omega$ , where  $\omega$  being the angular velocity. Therefore

$$\left(\frac{du}{d\theta}\right)^2 + u^2 = \frac{2}{h^2} \left[ A_0 u + \frac{A_1}{3} u^3 + \dots + \frac{A_n}{2n+1} u^{2n+1} \right] + \frac{\mu^2}{h^2} + E$$

where  $E$  is the constant of integration. We can get the value of  $E$  by putting the initial conditions, i.e.,  $u = u_0 = \frac{1}{a}$ ,  $\frac{du}{d\theta} = 0$ , we get

$$\left(\frac{du}{d\theta}\right)^2 = \frac{2}{h^2} \left[ A_0 (u - u_0) + \frac{A_n}{2n+1} (u^{2n+1} - u_0^{2n+1}) \right] + \frac{\mu^2}{h^2} \\ \left( \frac{1}{u^2} - \frac{1}{u_0^2} \right) + u_0^2 - u^2$$

Putting

$$2 \cdot \frac{2\pi}{\omega^2} \rho_0 \alpha_0 = m$$

where  $m$  is +ve and less than 1. On substituting the values of  $\rho_0$ ,  $\Pi$ ,  $\alpha_0$  and  $\omega^2$ , we see that  $m$  is actually less than 1, i.e.,  $m < 1$

$$\left(\frac{du}{d\theta}\right)^2 = mu_0 (1 - e^2)^{\frac{1}{2}} \left[ (u - u_0) + \frac{\alpha_1 e^2}{3\alpha_0 u_0^3} (u^3 - u_0^3) + \dots \right] \\ + \frac{\mu^2}{h^2} \left( \frac{1}{u^2} - \frac{1}{u_0^2} \right) + u_0^2 - u^2$$

By keeping terms only up to  $e^2$  we have

$$\left(\frac{du}{d\theta}\right)^2 = (u_0 - u) \left[ u + u_0 (1 - m) + \frac{\mu^2 (u + u_0)}{h^2 u_0^3 u^{\frac{1}{2}}} \right] \\ \left[ 1 - \frac{mu_0 e^2 \left\{ \frac{\alpha_1}{3\alpha_0 u_0} (u^2 + uu_0 + u_0^2) - \frac{1}{2} \right\}}{u + u_0 (1 - m) + \frac{\mu^2 (u + u_0)}{h^2 u_0^3 u^{\frac{1}{2}}}} \right]$$

or

$$\int \frac{du}{(u_0 - u)^{\frac{1}{2}} \left[ u + u_0 (1 - m) + \frac{\mu^2 (u + u_0)}{h^2 u_0^3 u^{\frac{1}{2}}} \right]^{\frac{1}{2}} + \dots} \\ + \frac{1}{2} mu_0 e^2 \int \frac{\left\{ \frac{\alpha_1}{3\alpha_0 u_0} (u^2 + uu_0 + u_0^2) - \frac{1}{2} \right\} du}{(u_0 - u)^{\frac{1}{2}} \left[ u + u_0 (1 - m) + \frac{\mu^2 (u + u_0)}{h^2 u_0^3 u^{\frac{1}{2}}} \right]^{\frac{1}{2}}} = \theta + c$$

By keeping only up to  $\mu^2$  the 1st part can be put in the form of

$$\int \frac{du}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} - \frac{\mu^2}{2h^2 u_0^2} \left\{ \int \frac{du}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} \right. \\ \left. + \int \frac{u_0 du}{u_0^2 (u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} \right\}$$

These on integration give

$$\sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} - \frac{\mu^2 m}{h^2 u_0^2 (1 - m)} \log \left\{ \frac{\sqrt{u + u_0(1 - m)} + \sqrt{(1 - m)(u_0 - u)}}{\sqrt{u}} \right\} \\ + \frac{\mu^2 m}{h^2 u_0^2 (2 - m)(1 - m)} \sqrt{\frac{u_0 - u}{u + u_0(1 - m)}} + \frac{\mu}{2h^2 u_0^2 (1 - m)^{\frac{3}{2}}} \frac{\sqrt{[u + u_0(1 - m)](u_0 - u)}}{u}$$

Now we take the 2nd part i.e.

$$mu_0 e^2 \int \frac{\left\{ \frac{\alpha_1}{3\alpha_0 u_0^2} (u^2 + uu_0 + u_0^2) - \frac{1}{2} \right\} du}{(u_0 - u)^{\frac{1}{2}} \left[ u + u_0(1 - m) + \frac{\mu^2 (u + u_0)}{h^2 u_0^2 u^2} \right]^{\frac{1}{2}}}$$

By keeping terms only up to  $\mu^2$  we have

$$\frac{1}{2} mu_0 e^2 \frac{\alpha_1}{3\alpha_0 u_0^2} \left[ \int \frac{(u^2 + uu_0 + u_0^2) du}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} \right. \\ \left. - \frac{\mu^2}{h^2 u_0^2} \int \frac{(u^2 + uu_0 + u_0^2)(u + u_0) du}{u^2 (u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} \right] \\ - \frac{mu_0 e^2}{u} \left[ \int \frac{du}{(u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}} \right]^2 - \frac{3\mu^2}{h^2 u_0^2} \int \frac{(u + u_0) du}{u^2 (u_0 - u)^{\frac{1}{2}} [u + u_0(1 - m)]^{\frac{1}{2}}}$$

These on integration give

$$e^2 \left[ \frac{mu_0 \alpha_1}{3\alpha_0 u_0^2} \left\{ -\frac{\sqrt{(u_0 - u)[u + u_0(1 - m)]}}{2} + \frac{1}{2} mu_0 \sin^{-1} \frac{2u - mu_0}{(2 - m)u_0} \right\} \right. \\ \left. - \frac{u}{(2 - m)} \left\{ \frac{\alpha_1}{3\alpha_0} (1 + m^2 - m) - \frac{1}{2} \right\} \sqrt{\frac{u_0 - u}{u + u_0(1 - m)}} - \frac{\alpha_1 m^2 \mu^2}{2\alpha_0 h^2 u_0^2 (1 - m)} \sqrt{\frac{u_0 - u}{u + u_0(1 - m)}} \right. \\ \left. + \frac{\alpha_1 m \mu^2}{2\alpha_0 h^2 u_0^2 (1 - m)} \log \left\{ \frac{\sqrt{u + u_0(1 - m)} + \sqrt{(1 - m)(u_0 - u)}}{\sqrt{u}} \right\} \right. \\ \left. - \frac{\alpha_1 m \mu^2 (1 + m^2 - m)}{2\alpha_0 h^2 u_0^2 (1 - m)(2 - m)} \left\{ \frac{1}{2} \left[ \frac{u_0 - u}{u + u_0(1 - m)} \right]^{\frac{1}{2}} + \sqrt{\frac{u_0 - u}{u + u_0(1 - m)}} \right\} \right]$$

$$\begin{aligned}
& -\frac{\alpha_1}{2\alpha_0} \frac{m\mu^2(1+m)}{h^2 u_0^4 (1-m)^{\frac{3}{2}}} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& + \frac{\alpha_1 m \mu^2}{2\alpha_0 h^2 u_0^4 (1-m)^{\frac{3}{2}}} \left[ \frac{\sqrt{\{u+u_0(1-m)\}(1-m)(u_0-u)}}{2u} \right. \\
& \quad \left. - \frac{2-m}{2} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \right] \\
& + \frac{\alpha_1 m \mu^2}{2\alpha_0 h^2 u_0^4 (1-m)^{\frac{3}{2}}} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& + \frac{\alpha_1 \mu^2 m(1+m)}{2\alpha_0 h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} + \frac{\alpha_1 m \mu^2 (1+m^2-m)}{2\alpha_0 h^2 u_0^4 (1-m)^2 (2-m)^2} \\
& \left[ \frac{1}{2} \left\{ \frac{u_0-u}{u+u_0(1-m)} \right\}^{\frac{1}{2}} + \sqrt{\frac{u_0-u}{u+u_0(1-m)}} \right] + \frac{3}{2} \frac{m \mu^2}{h^2 u_0^4 (1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} \\
& - \frac{1}{4} \frac{m \mu^2}{h^2 u_0^4 (1-m)(2-m)} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} + \frac{3}{2} \frac{m \mu^2}{h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} \\
& - \frac{1}{2} \frac{m \mu^2}{h^2 u_0^4 (1-m)^{\frac{3}{2}}} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& + \frac{1}{2} \frac{\mu^2 m}{h^2 u_0^4 (2-m)^2 (1-m)^{\frac{3}{2}}} \left[ \frac{1}{2} \left\{ \frac{(u_0-u)(1-m)}{u+u_0(1-m)} \right\}^{\frac{1}{2}} - \sqrt{\frac{(u_0-u)(1-m)}{u+u_0(1-m)}} \right] \\
& - \frac{3}{2} \frac{\mu^2 m}{h^2 u_0^4 (1-m)^2} \sqrt{\frac{(u+u_0(1-m))(u_0-u)}{u}} \\
& \quad + \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& \left\{ \frac{m}{4} + 1 \right\} \frac{3\mu^2 m}{2h^2 u_0^4 (1-m)^{\frac{3}{2}}} - \frac{3}{2} \frac{\mu^2 m}{h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} \\
& - \frac{1}{4} \frac{\mu^2 m}{h^2 u_0^4 (2-m)^2 (1-m)^{\frac{3}{2}}} \left[ \frac{1}{2} \left\{ \frac{(u_0-u)(1-m)}{u+u_0(1-m)} \right\}^{\frac{1}{2}} - \sqrt{\frac{(1-m)(u_0-u)}{u+u_0(1-m)}} \right] \\
& - \frac{1}{4} \frac{\mu^2 m}{h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}}
\end{aligned}$$

Thus we have

$$\theta + c = \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{8}{2h^2 u_0^4 (1-m)^{\frac{3}{2}}} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\}$$

$$\begin{aligned}
& + \frac{\mu^2 m}{h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} + \frac{\mu^2}{2h^2 u_0^4 (1-m)^2} \frac{\sqrt{(u_0-u)(u+u_0)(1-m)}}{u} \\
& + e^2 \left[ \frac{m^2}{4} \frac{\alpha_1}{\alpha_0} \sin^{-1} \frac{2u-mu_0}{(2-m)u_0} + \left\{ - \left[ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right] \frac{m}{(2-m)} \right. \right. \\
& + \frac{\mu^2 m}{2h^2 u_0^4 (1-m)^2 (2-m)^2} \left[ \frac{\alpha_0}{\alpha_0} (2-2m-3m^2+5m^2) - 3(1+m-m^2) \right] \left. \right\} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} \\
& - \frac{mu_0 \alpha_1}{3\alpha_0 u_0^2} \cdot \frac{\sqrt{(u_0-u)(u+u_0(1-m))}}{2} \\
& + \frac{m\mu^2}{4h^2 u_0^4 (1-m)^2} \left( \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right) \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& + \frac{m^2 \mu^2}{2h^2 u_0^4 (1-m)^2 (2-m)^2} \left\{ \frac{(1+m^2-m)\alpha_1}{3\alpha_0} - \frac{1}{2} \right\} \left[ \frac{u_0-u}{u+u_0(1-m)} \right]^{\frac{1}{2}} \\
& + \frac{m\mu^2}{4h^2 u_0^4 (1-m)^2} \left( \frac{\alpha_1}{\alpha_0} - \frac{1}{2} \right) \frac{\sqrt{(u+u_0(1-m))(u_0-u)}}{u} \Big] + c
\end{aligned}$$

where  $c$  is the constant of integration. We can get the value of the constant by noticing the initial conditions, i.e.,  $u=u_0$  and  $\theta=0$ , we have

$$c = \frac{\pi}{2} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m}{4h^2 u_0^4 (1-m)^2} \log \{ 2-m \} \left[ \frac{e^2}{2(1-m)} \left\{ \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right\} - 3 \right]$$

Hence, we have

$$\begin{aligned}
& \theta + \frac{\pi}{2} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m}{4h^2 u_0^4 (1-m)^2} \log (2-m) \left[ \frac{e^2}{2(1-m)} \left\{ \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right\} - 3 \right] \\
& = \sin^{-1} \frac{2u-mu_0}{(2-m)u_0} - \frac{\mu^2 m}{2h^2 u_0^4 (1-m)^2} \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \\
& + e^2 \left[ - \frac{mu_0 \alpha_1}{3\alpha_0 u_0^2} \frac{\sqrt{(u_0-u)(u+u_0(1-m))}}{2} + \frac{m^2}{4} \frac{\alpha_1}{\alpha_0} \sin^{-1} \frac{2u-mu_0}{(2-m)u_0} \right. \\
& + \left\{ - \left[ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right] \frac{m}{2-m} + \frac{\mu^2 m}{2h^2 u_0^4 (1-m)^2 (2-m)^2} \left[ \frac{\alpha_1}{\alpha_0} (2-2m-3m^2+5m^2) - \right. \right. \\
& \left. \left. 3(1+m-m^2) \right] \right\} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} + \frac{m\mu^2}{4h^2 u_0^4 (1-m)^2} \left( \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right) \cdot \\
& \left. \log \left\{ \frac{\sqrt{u+u_0(1-m)} + \sqrt{(1-m)(u_0-u)}}{\sqrt{u}} \right\} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{m^2 \mu^2}{2h^2 u_0^4 (1-m)^2 (2-m)^2} \left\{ (1+m^2-m) \frac{\alpha_1}{3\alpha_0} - \frac{1}{2} \right\} \left[ \frac{u_0-u}{u+u_0(1-m)} \right]^{\frac{1}{2}} \\
& + \frac{m\mu^2}{4h^2 u_0^4 (1-m)^2} \left( \frac{\alpha_1}{\alpha_0} - \frac{1}{2} \right) \frac{\sqrt{(u+u_0(1-m))(u_0-u)}}{u} + \\
& \frac{\mu^2 m}{h^2 u_0^4 (2-m)(1-m)^2} \sqrt{\frac{u_0-u}{u+u_0(1-m)}} + \frac{\mu^2}{2h^2 u_0^4 (1-m)^2} \frac{\sqrt{(u_0-u)(u+u_0(1-m))}}{u}
\end{aligned}$$

To see how the ejected particle behaves at a sufficiently great distance we expand the above terms in powers of  $\frac{u}{u_0}$  and keeping the terms only up to  $\frac{u}{u_0}$ , neglecting its 2nd and higher powers and also neglecting 3rd and higher powers of  $\left(\frac{m}{2-m}\right)$  as  $m$  is small

Thus we have

$$\begin{aligned}
& \theta + \frac{\pi}{2} \left( \frac{1+e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m}{4h^2 u_0^4 (1-m)^{\frac{1}{2}}} \log(2-m) \left[ \frac{e^2}{2(1-m)} \left\{ \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right\} - 3 \right] \\
& = \frac{2u-mu_0}{(2-m)u_0} + \frac{\mu^2 m(3m-4)}{2h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \left( 1 - \frac{u}{2u_0} \cdot \frac{2-m}{1-m} \right) \\
& - \frac{3}{2} \frac{\mu^2 m}{h^2 u_0^4 (1-m)^{\frac{1}{2}}} \cdot \frac{2-m}{1-m} \cdot \frac{u}{u_0} + \frac{\mu^2}{2h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left[ u_0 + \frac{m}{2(1-m)} - \frac{u}{u_0} \left( \frac{2-m}{1-m} \right)^{\frac{1}{2}} \right] \\
& + e^2 \left[ \left\{ \frac{m\mu^2}{8h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right) \cdot \frac{2-m}{1-m} \cdot \frac{u}{u_0} + \right. \right. \\
& \left. \left\{ - \left[ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right] \cdot \frac{m}{2-m} + \frac{\mu^2 m}{4h^2 u_0^4 (2-m)^2 (1-m)^2} \right. \right. \\
& \left. \left. \left[ \frac{\alpha_1}{\alpha_0} (4-24m+30m^2-11m^3) + \frac{3}{2} (4-6m^2+3m^3) \right] \right\} \frac{1}{\sqrt{1-m}} \left( 1 - \frac{u}{u_0} \cdot \frac{2-m}{1-m} \right) \right. \\
& \left. - \frac{m\alpha_1}{6\alpha_0} (1-m)^{\frac{1}{2}} \left\{ 1 + \frac{m}{2(1-m)} \cdot \frac{u}{u_0} \right\} + \frac{m^2 \alpha_1}{4 \alpha_0} \cdot \frac{2u-mu_0}{(2-m)u_0} \right. \\
& \left. + \frac{m^2 \mu^2}{2h^2 u_0^4 (1-m)^2 (2-m)^2} \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \frac{1}{(1-m)^{\frac{1}{2}}} \left\{ 1 - \frac{3}{2} \frac{u}{u_0} \cdot \frac{2-m}{1-m} \right\} \right. \\
& \left. + \frac{m\mu^2}{4h^2 u_0^4 (1-m)^2} \left( \frac{\alpha_1}{\alpha_0} - \frac{1}{2} \right) \left\{ \frac{u_0}{u} + \frac{m}{2(1-m)} - \frac{u}{u_0} \cdot \frac{1}{2} \left( \frac{2-m}{1-m} \right)^{\frac{1}{2}} \right\} \right]
\end{aligned}$$

With further simplification, we get

$$\theta + \frac{\pi}{2} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m}{4h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left[ \frac{e^2}{2(1-m)} \left\{ \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right\} - 3 \right] \log(2-m)$$

$$\begin{aligned}
& + \frac{m}{(2-m)} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m(6-5m)}{4h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} - e^2 \left[ - \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \right. \\
& \quad \left. \frac{m}{(2-m)(1-m)^{\frac{1}{2}}} \right. \\
& + \frac{\mu^2 m}{4h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{\alpha_0} (4-24m+30m^2-11m^3) + \frac{1}{2} (4-6m^2+3m^3) \right\} \\
& + \frac{m^2 \mu^2}{2h^2 u_0^4 (2-m)^2 (1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \left. \right] + e^2 m(1-m)^{\frac{1}{2}} \frac{\alpha_1}{6\alpha_0} \\
& - \frac{m^2 \mu^2 e^2}{8h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{3}{2} \right) \\
& = \frac{u}{u_0} \left[ \frac{2}{(2-m)} - \frac{\mu^2 (2+2m)^2}{16h^2 u_0^4 (1-m)^2} + e^2 \left\{ \frac{m\mu^2 (2-m)}{8h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right) \right. \right. \\
& + \left. \left[ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right] \frac{m}{2(1-m)^{\frac{1}{2}}} - \frac{\mu^2 m}{8h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \left[ \frac{\alpha_1}{\alpha_0} (4-24m+ \right. \right. \\
& \left. \left. 30m^2-11m^3) + \frac{1}{2} (4-6m+3m^2) \right] - \frac{m^2 \mu^2}{h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \right. \\
& \left. \left. - \frac{m^2 \alpha_1}{12\alpha_0 (1-m)^{\frac{1}{2}}} + \frac{m^2}{2} \cdot \frac{\alpha_1}{\alpha_0} \cdot \frac{1}{2-m} - \frac{m\mu^2 (2-m)^2}{32h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{3}{2} \right) \right\} \right] \\
& + \frac{u}{u_0} \left[ \frac{\mu^2}{2h^2 u_0^4 (1-m)^{\frac{1}{2}}} + \frac{m e^2 \mu^2}{4h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{3}{2} \right) \right]
\end{aligned}$$

We introduce new constants

$$\begin{aligned}
K &= \frac{\pi}{2} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m}{4h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left[ \frac{e^2}{2(1-m)} \left( \frac{6+9m}{2} - \frac{5m\alpha_1}{\alpha_0} \right) - 3 \right] \log(2-m) \\
& + \frac{m}{(2-m)} \left( 1 + \frac{e^2 m^2 \alpha_1}{4\alpha_0} \right) + \frac{\mu^2 m(6-5m)}{4h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \\
& - e^2 \left[ - \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \frac{m}{(2-m)(1-m)^{\frac{1}{2}}} \right. \\
& + \frac{\mu^2 m}{4h^2 u_0^4 (2-m)(1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{\alpha_0} (4-24m+30m^2-11m^3) + \frac{1}{2} (4-6m^2+3m^3) \right\} \\
& + \frac{m^2 \mu^2}{2h^2 u_0^4 (2-m)^2 (1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} - \frac{\alpha_1 m(1-m)^{\frac{1}{2}}}{6\alpha_0} \\
& \left. + \frac{m^2 \mu^2}{8h^2 u_0^4 (1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{3}{2} \right) \right].
\end{aligned}$$



$$\begin{aligned}
B = & \frac{2}{2-m} - \frac{\mu^2(2+m)^2}{16h^2n_0^4(1-m)^{\frac{1}{2}}} + e^2 \left[ \frac{m\mu^2(2-m)}{8h^2n_0^4(1-m)^{\frac{1}{2}}} \left( \frac{6+9m}{2} - 5\frac{m\alpha_1}{\alpha_0} \right) \right. \\
& + \left. \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} \frac{m}{2(1-m)^{\frac{1}{2}}} \right. \\
& - \frac{\mu^2 m}{8h^2n_0^4(2-m)(1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{\alpha_0} (4-24m+30m^2-11m^3) + \frac{1}{2} (4-6m^2+3m^3) \right\} \\
& - \frac{m^2\mu^2}{h^2n_0^4(2-m)(1-m)^{\frac{1}{2}}} \left\{ \frac{\alpha_1}{3\alpha_0} (1+m^2-m) - \frac{1}{2} \right\} - \frac{m^2\alpha_1}{12\alpha_0(1-m)^{\frac{1}{2}}} \\
& \left. + \frac{m^2}{2} \frac{\alpha_1}{\alpha_0(2-m)} - \frac{m\mu^2(2-m)^2}{32h^2n_0^4(1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{1}{2} \right) \right]
\end{aligned}$$

and

$$C = \frac{\mu^2}{2h^2n_0^4(1-m)^{\frac{1}{2}}} + \frac{m\mu^2e^2}{4h^2n_0^4(1-m)^{\frac{1}{2}}} \left( \frac{\alpha_1}{\alpha_0} - \frac{1}{2} \right)$$

where

$$K > 1$$

$$B \leq 1$$

and

$$C < 1$$

Hence, the path is simplified to

$$\theta + K = B \frac{u''}{u_0} + C \frac{u_0''}{u}$$

Now  $\frac{u''}{u_0}$  is small, and  $\frac{u_0''}{u}$  is therefore very great

Therefore  $C \frac{u_0''}{u}$  is the dominating term which will give the main part of the curve. Thus we consider  $C \frac{u_0''}{u} = \theta + K$  which gives a deformed spiral of Archimedes

In the end I think it my great privilege to record my grateful thanks to Prof A. C. Banerji, for his keen interest in the preparation of this paper

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## TWO SELF-RECIPROCAL FUNCTIONS

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1 The object of this paper is to investigate functions which are self-reciprocal in the Hankel transform of order  $\nu$  and following Hardy and Littlewood we shall call such functions  $R_\nu$ . The functions are obtained by the application of the theorem<sup>1</sup> that if  $f(y)$  is  $R_1$ , then the function

$$g(x) = \int_0^\infty f(y) (xy)^{-\frac{1}{2}} H_{\frac{1}{2}(\nu-1)}(xy) dy \quad (1.1)$$

is  $R_\nu$ , where  $H_\nu(x)$  is Struve's function defined by

$$\begin{aligned} H_\nu(x) &= \sum_{r=0}^{\infty} \frac{(-1)^r x^{\nu+2r+1}}{2^{\nu+2r+1} \Gamma(r+\frac{1}{2}) \Gamma(\nu+r+\frac{1}{2})} \\ &= (\frac{1}{2}x)^{\nu+1} {}_1F_2(1, \frac{1}{2}, \nu+\frac{3}{2}, -\frac{1}{4}x^2) \end{aligned}$$

It is interesting to note that the  $R_\nu$  functions investigated in this paper are in the form of generalised hypergeometric function  ${}_2F_3$ .

2 We know<sup>2</sup> that  $x^{\nu+\frac{1}{2}} e^{-\frac{1}{2}x^2} T_0^*(x^2)$  is  $R_\nu$  or skew  $R_\nu$  according as  $\nu$  is even or odd. Let us take  $\nu=1$  and  $n$  to be an even integer. Then

$$f(y) = y^{\frac{1}{2}} e^{-\frac{1}{2}y^2} T_1^*(y^2)$$

is  $R_1$ . Taking this value of  $f(y)$  in (1.1), we have

$$g(x) = \int_0^\infty (xy)^{-\frac{1}{2}} H_{\frac{1}{2}(\nu-1)}(xy) y^{\frac{1}{2}} e^{-\frac{1}{2}y^2} T_1^*(y^2) dy \quad (2.1)$$

$$= \int_0^\infty \sum_{r=0}^{\infty} \left[ \frac{(-1)^r (xy)^{\nu+\frac{1}{2}} \{y^{\frac{1}{2}} e^{-\frac{1}{2}y^2} T_1^*(y^2)\}}{2^{\nu+2r+1} \Gamma(r+\frac{1}{2}) \Gamma(\frac{1}{2}\nu+r+1)} \right] dy \quad (2.2)$$

Now the series for  $y^{-\frac{1}{2}v-\frac{1}{2}} H_{\frac{1}{2}(v-1)}(y)$  is uniformly convergent in any arbitrary interval of values of  $y$  and the function

$$y^{\frac{1}{2}} e^{-\frac{1}{2}y^2} T_1''(y^2)$$

is continuous. Also the integral (2'1) is absolutely convergent. Hence we may integrate the series in (2.2) term by term. Thus

$$g(y) = \frac{y^{\frac{1}{2}} 2^{-\frac{1}{2}v}}{\Gamma(n+2)} \sum_{r=0}^{\infty} \frac{(-\frac{1}{2}y^2)^r}{\Gamma(r+\frac{1}{2}) \Gamma(\frac{1}{2}v+r+1) \Gamma(\frac{1}{2}-r)} \sum_{s=0}^n \frac{(-)^s \Gamma(\frac{1}{2}+s-r) \Gamma(n-s+r+\frac{1}{2})}{s! (n-s)!},$$

where we have used an integral due to Varma.<sup>3</sup>

If we use the formula  $\Gamma(x) \Gamma(1-x) = x \operatorname{cosec} \pi x$ , it is easy to see, after some simplification, that the function

$$y^{\frac{1}{2}} \sum_{s=0}^n {}^nC_{s, \frac{1}{2}} F_s \left( \frac{1}{2}, n-s+\frac{1}{2}, \frac{1}{2}-s, -\frac{1}{2}y^2 \right)$$

is  $R_2$ .

3 Taking<sup>4</sup> in (1'1)

$$f(y) = y^{-\frac{1}{2}} D^{\frac{1}{2}}{}_{1, m+1}(y),$$

which is  $R_1$ , we have

$$\begin{aligned} g(x) &= x^{-\frac{1}{2}v} \int_0^{\infty} y^{-\frac{1}{2}(v+1)} D^{\frac{1}{2}}{}_{1, m+1}(y) H_{\frac{1}{2}(v-1)}(xy) dy \\ &= x^{-\frac{1}{2}v} \int_0^{\infty} y^{-\frac{1}{2}(v+1)} D^{\frac{1}{2}}{}_{1, m+1}(y) \sum_{r=0}^{\infty} \frac{(-1)^r (xy)^{v+\frac{1}{2}r+1}}{2^{v+\frac{1}{2}r+1} \Gamma(r+\frac{1}{2}) \Gamma(\frac{1}{2}v+r+1)} dy \\ &= \sum_{r=0}^{\infty} \frac{(\frac{1}{2}x)^{v+\frac{1}{2}r+1} 2^{-\frac{1}{2}v}}{\Gamma(r+\frac{1}{2}) \Gamma(\frac{1}{2}v+r+1)} \int_0^{\infty} y^{2r} D^{\frac{1}{2}}{}_{1, m+1}(y) dy, \end{aligned}$$

term by term integration being easily justified. Since<sup>5</sup>

$$D^{\frac{1}{2}}{}_{1, m+1}(y) = D_0(y) \sum_{r=0}^{2m+1} \frac{\{(2m+1)\}^2}{(s!)^2 (2m+1-s)!} D_{2r}(y)$$

we have

$$\begin{aligned}
 g(x) &= \sum_{r=0}^{\infty} \sum_{s=0}^{2m+1} \frac{(\frac{1}{2}x)^{s+r+1} 2^{-\frac{1}{2}r} \{(2m+1)!\}^2}{\Gamma(r+\frac{1}{2}) \Gamma(\frac{1}{2}v+r+1) (s!)^2 (2m+1-s)!} \int_0^{\infty} y^{2r} D_0(y) D_{s,1}(y) dy \\
 &= \sum_{r=0}^{2m+1} \sum_{s=0}^{\infty} \frac{\{(2m+1)!\}^2 2^{r-\frac{1}{2}v-1} x}{(r!)^2 (2m+1-r)! s!} \frac{\{\Gamma(s+1)\}^2 \Gamma(s+\frac{1}{2})}{\Gamma(s+\frac{1}{2}) \Gamma(s+\frac{1}{2}v+1) \Gamma(s-r+1)} (-\frac{1}{2}x)^s,
 \end{aligned}$$

where we have used an integral due to Watson<sup>6</sup>

We therefore conclude that the function

$$\sum_{r=0}^{2m+1} \frac{2^r x}{(r!)^2 (2m+1-r)! \Gamma(1-r)} {}_2F_2\left(\frac{1}{2}, 1, 1, \frac{1}{2}, \frac{1}{2}v+1, 1-r, -\frac{1}{2}x^2\right)$$

is  $R$ .

My best thanks are due to Dr R. S. Varma for suggesting the problem and for his guidance in the preparation of this paper

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# AN INFINITE INTEGRAL INVOLVING WHITTAKER'S FUNCTION

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The object of this paper is to investigate an infinite integral involving Whittaker's function  $W_{k,m}(x)$ . The method adopted is that of integration by parts and it is interesting to note that this simple method gives a pretty general result.

We start with the following integral due to Erdelyi<sup>1</sup>

$$\Gamma(\nu-2m+1) x^{\frac{1}{2}(m-k-1)} e^{\frac{1}{2}x} W_{\frac{1}{2}(k+3m-\nu-\frac{1}{2}), \frac{1}{2}(\nu+k-m+\frac{1}{2})}(x) \\ = \int_0^{\infty} y^{\frac{1}{2}\nu-m-\frac{1}{2}} e^{\frac{1}{2}y} J_{\nu}(2\sqrt{xy}) W_{k,m}(y) dy. \quad (1)$$

$$R(\nu+1) > 0, R(\nu-2m+1) > 0 \text{ and } R(2m-2k-\nu) > -\frac{1}{2} \\ = I, \text{ say}$$

Using the relation<sup>2</sup>

$$\left(\frac{d}{dy}\right)^{2s} \left[ y^{-\frac{1}{2}+m+s} e^{\frac{1}{2}y} W_{k+s, m+s}(y) \right] \\ = \binom{-\frac{1}{2}+k+m+2s}{2s} y^{-\frac{1}{2}+m} e^{\frac{1}{2}y} W_{k,m}(y)$$

where

$$\binom{\alpha}{p} = \alpha(\alpha-1)(\alpha-2) \dots (\alpha-p+1)$$

We can write (1) in the form

$$I = \frac{\Gamma(\frac{1}{2}+k+m)}{\Gamma(k+m+2s+\frac{1}{2})} \int_0^{\infty} \left\{ y^{\frac{1}{2}\nu-2m} J_{\nu}(2\sqrt{xy}) \right\} \\ \times \left(\frac{d}{dy}\right)^{2s} \left\{ y^{-\frac{1}{2}+m+s} e^{\frac{1}{2}y} W_{k+s, m+s}(y) \right\} dy$$

Integrating the left-hand side by parts and noting that

$$y^{4\nu-2m} J_\nu \left( 2\sqrt{xy} \right) = \sum_{r=0}^{\infty} \frac{(-)^r x^{4\nu+r}}{r! \Gamma(\nu+r+1)} y^{r-2m+r},$$

and hence,

$$\begin{aligned} & \left( \frac{d}{dy} \right)^{2s} \left\{ y^{4\nu-2m} J_\nu \left( 2\sqrt{xy} \right) \right\} \\ &= x^{4\nu} y^{\nu-2m-2s} \sum_{r=0}^{\infty} \frac{(-xy)^r \Gamma(\nu-2m+r+1)}{r! \Gamma(\nu+r+1) \Gamma(\nu-2m+r-2s+1)} \\ &= x^{4\nu} y^{\nu-2m-2s} \frac{\Gamma(\nu-2m+1)}{\Gamma(\nu+1) \Gamma(\nu-2m-2s+1)} \\ &\quad \times {}_1F_2 \left( \nu-2m+1, \nu+1, \nu-2m-2s+1, -xy \right), \end{aligned}$$

we get that

$$\begin{aligned} I &= \frac{\Gamma(\frac{1}{2}+k+m) \Gamma(\nu-2m+1) x^{4\nu}}{\Gamma(\nu+1) \Gamma(k+m+2s+\frac{1}{2}) \Gamma(\nu-2m-2s+1)} \int_0^\infty y^{\nu-2m-2s} \\ &\quad \times {}_1F_2 \left[ \nu-2m+1, \nu+1, \nu-2m-2s+1, -xy \right] e^{4y} y^{-\frac{1}{2}+m+s} W_{k+s, m+s}(y) dy \end{aligned}$$

Hence we obtain that

$$\begin{aligned} & W_{\frac{1}{2}(k+m-\nu-\frac{1}{2}), \frac{1}{2}(\nu+k-m+\frac{1}{2})}(x) = e^{-\frac{1}{2}x} x^{\frac{1}{2}(\nu-m+\frac{1}{2}k+\frac{1}{2})} \\ &\quad \times \frac{\Gamma(\frac{1}{2}-k+m) \Gamma(\frac{1}{2}+k+m)}{\Gamma(\nu+1) \Gamma(\nu-2m-2s+\frac{1}{2}) \Gamma(k+m+2s+\frac{1}{2})} \int_0^\infty y^{\nu-m-s-\frac{1}{2}} e^{4y} W_{k+s, m+s}(y) \\ &\quad \times {}_1F_2 \left[ \nu-2m+1, \nu+1, \nu-2m-2s+1, -xy \right] dy \end{aligned}$$

valid when  $s$  is a positive integer,  $R(\nu+1) > 0$ ,  $R(\nu-2m+1) > 0$ , and  $R(2m-2k-\nu+\frac{1}{2}) > 0$

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# ON SELF-RECIPROCAL FUNCTIONS

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We know<sup>1</sup> that if  $f(x)$  is  $R_\mu$ , then

$$g(x) = \int_0^\infty \frac{x^{\nu+\frac{1}{2}}}{(x^2+n^2)^{\frac{1}{2}\mu+\frac{1}{2}\nu+1}} f(n) \cdot dn \quad (1)$$

is  $R_\nu$

For  $\mu = -\frac{1}{2}$ ,  $\nu = \frac{1}{2}$ , this gives<sup>2</sup> that

$$g(p) = p \int_0^\infty \frac{f(y)}{y^{\frac{1}{2}} + p^{\frac{1}{2}}} dy \quad (2)$$

is  $R_\nu$ , if  $f(x)$  is  $R_\mu$

In the present paper I have used this result to deduce some functions which are self-reciprocal in the sine transform

(1) The function

$$f(x) = \frac{\cos\left(\frac{1}{2}x^2 - \frac{\pi}{8}\right)}{\sin\left(\frac{1}{2}x^2 - \frac{\pi}{8}\right)} \text{ is } \pm R_0$$

Using this function in (2), we get that the function

$$\frac{\cos\left(\frac{1}{2}p^2 + \frac{\pi}{8}\right)}{\sin\left(\frac{1}{2}p^2 + \frac{\pi}{8}\right)} \text{ is } \pm R_0$$

(2) Using

$$f(x) = \frac{1}{\cosh\left(x\sqrt{\frac{\pi}{2}}\right)} \text{ in (2),}$$

$$g(p) = p \int_0^\infty \frac{dy}{(y^2 + p^2) \cosh\left(y\sqrt{\frac{\pi}{2}}\right)}$$

Evaluating this integral, we get that

$$g(p) = \frac{\pi}{2 \cos\left(p\sqrt{\frac{\pi}{2}}\right)} + \sum_{n=0}^\infty \frac{2\sqrt{2\pi} (-1)^n p}{2p^2 - \pi (2n+1)^2}$$

is  $R_0$

$$(3) \text{ Taking } f(x) = \frac{\cosh \left( \frac{1}{2} x \sqrt{\pi} \right)}{\cosh \left( x \sqrt{\pi} \right)}$$

we get that

$$\begin{aligned} g(p) &= p \int_0^{\infty} \frac{\cosh \left( \frac{1}{2} y \sqrt{\pi} \right)}{(y^2 + p^2) \cosh \left( y \sqrt{\pi} \right)} dy \\ &= \frac{\pi}{2} \frac{\cos \left( \frac{1}{2} p \sqrt{\pi} \right)}{\cos \left( p \sqrt{\pi} \right)} + 4 \sqrt{\pi} p \sum_{n=0}^{\infty} \frac{(-1)^n \cos \left( \frac{1}{2} n \pi + \frac{\pi}{4} \right)}{4p^2 - (2n+1)^2 \pi} \end{aligned}$$

is R,

$$(4) \text{ Taking } f(x) = \frac{\sinh \left( x \sqrt{\frac{\pi}{6}} \right)}{\sinh \left( x \sqrt{\frac{3\pi}{2}} \right)},$$

$$\begin{aligned} g(p) &= p \int_0^{\infty} \frac{\sinh \left( y \sqrt{\frac{\pi}{6}} \right)}{(y^2 + p^2) \sinh \left( y \sqrt{\frac{3\pi}{2}} \right)} dy \\ &= \frac{\pi}{2} \frac{\sin \left( p \sqrt{\frac{\pi}{6}} \right)}{\sin \left( p \sqrt{\frac{3\pi}{2}} \right)} + \sqrt{6} \pi p \sum_{n=0}^{\infty} \frac{(-1)^{n+1} \sin \frac{1}{2} n \pi}{3p^2 - 2n^2 \pi} \end{aligned}$$

is R,

$$(5) \text{ Taking } f(x) = \frac{\cos \frac{1}{2} x^2 + \sin \frac{1}{2} x^2}{\cosh \left( x \sqrt{\frac{\pi}{2}} \right)},$$

we get that

$$\begin{aligned} g(p) &= p \int_0^{\infty} \frac{\cos \frac{1}{2} y^2 + \sin \frac{1}{2} y^2}{(y^2 + p^2) \cosh \left( y \sqrt{\frac{\pi}{2}} \right)} dy \\ &= \frac{\pi}{2} \frac{\cos \frac{1}{2} p^2 - \sin \frac{1}{2} p^2}{\cos \left( p \sqrt{\frac{\pi}{2}} \right)} \end{aligned}$$

is R,

I am indebted to Dr. R. S. Varma for his helpful suggestions

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# RADIAL OSCILLATIONS OF THE GENERALISED ROCHE'S MODEL

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## SUMMARY

For small radial oscillations of the generalised Roche's model it has been found that the radius of the nucleus must bear certain defined ratios to that of the whole sphere and that only one mode is possible for a particular value of the ratio. The bearing of this on the origin of the spiral nebulae has been considered. The generalised Roche's model has further been shown incapable of large radial oscillations.

It is well known that the extreme limit of non-homogeneity is reached by the Roche's model, viz a small and intensely dense solid nucleus surrounded by an atmosphere of negligible density. The model so takes its name as it was extensively utilised by Roche in his researches on Cosmogony. As the whole of the mass is supposed concentrated at the centre, the density is infinite at the centre and zero elsewhere and in this respect the model resembles the polytropic one with index  $n=5$ . That the model is not a mathematical fiction but has a definite physical bearing, has been explained by Jeans.<sup>1</sup>

The small radial oscillations of Roche's model has been considered by Sterne,<sup>2</sup> who has obtained the periods of the different modes. P L Bhatnagar, in his unpublished thesis for the D Phil degree of the Allahabad University, has shown that the model is unstable for large radial oscillations.

In his researches on the stability of a rotating compressible gaseous mass, Jeans has established two distinct methods of breaking up of a rotating configuration (1) fissional and (2) equatorial. A rotating mass of small central condensation breaks up by fission, when a furrow forms near the middle and the pear-shaped figure divides into two detached masses. On the other hand, a rotating mass of great central condensation, e.g., the Roche's model, becomes lens-shaped and finally matter is shed from the equator in a continuous stream.

To bridge over the wide gap between the two extreme cases and effect a continuous transition from homogeneity to non homogeneity Jeans considered the generalised Roche's model<sup>10</sup> viz a nucleus of uniform finite density with an atmosphere of finite extent but of infinitesimal density. Jeans<sup>11</sup> established the quite general result that if the ratio of the volume of the atmosphere to that of the nucleus be less than one third the rotating mass will break up by fission otherwise equatorially.

We have in this paper considered the radial oscillations of the generalised Roche's model. For small oscillations we have found that the radius of the nucleus must bear certain defined ratios to that of the whole sphere and that only one mode is possible for a particular value of the ratio. We have calculated this ratio for the fundamental mode and we have found that the nucleus can at the most occupy about 30% of the volume of the whole sphere. The bearing of this on the origin of the spiral nebulae has been considered. Finally the generalised Roche's model has been shown incapable of large radial oscillations.

Let initially  $R$  be the radius and  $\rho$  the mean density of the model. Let the nucleus be of radius  $a$  and let there be a continuous density distribution  $\rho_0 = l/\xi_0^3$  in the annulus where  $\rho_0$  is the density at a point distant  $\xi_0$  from the centre and  $l$  is a constant which we shall presently allow to approach zero.

Now we have that mass inside the nucleus

$$= \frac{4\pi}{3} R^3 \rho - 4\pi l (R - a)$$

Hence we have that mass within the sphere of radius  $\xi_0$

$$= \frac{4\pi}{3} R^3 \rho - 4\pi l (R - \xi_0)$$

The value of gravity at  $\xi_0$  is

$$g_0 = \frac{G}{\xi_0^2} \left[ \frac{4\pi}{3} R^3 \rho - 4\pi l (R - \xi_0) \right]$$

The pressure at  $\xi_0$  is

$$\begin{aligned} p_0 &= 4\pi G l \left[ -\frac{R^3 \rho - 3lR}{9\xi_0^3} - \frac{k}{2\xi_0^2} \right]_{\xi_0}^R \\ &= 4\pi G l \left[ \frac{\rho}{9} \frac{R^3}{\xi_0^3} - \frac{kR}{9\xi_0} + \frac{l}{\xi_0^3} - \frac{\rho}{9} - \frac{k}{6R^2} \right] \end{aligned}$$

Now as  $h \rightarrow 0$ ,  $\rho_0$  and  $P_0$  separately approach 0 except in the nucleus, while

$$\left. \begin{aligned} q_0 &\rightarrow \frac{4\pi G}{3} \frac{R^3 \rho}{\xi_0^3}, \\ \frac{\rho_0}{P_0} &\rightarrow \frac{9x}{4\pi R^2 G \rho (1-x^3)}, \\ \text{where } \frac{\xi_0}{R} &= x, \\ \frac{q_0 \rho_0 \xi_0}{P_0} = \nu &\rightarrow \frac{3}{1-x^3}, \\ \frac{R^2 \rho_0 n^2}{P_0 \gamma} &\rightarrow \frac{9n^2 x}{4\pi G \gamma \rho (1-x^3)}, \\ \text{and } (\alpha R \rho_0 g_0 / P_0 x) &\rightarrow 3\alpha/x^2 (1-x^3), \end{aligned} \right\} \quad (1)$$

where  $\alpha = 3 - 4/\gamma$ ,  $\gamma$  being the ratio of the specific heats (regarding matter and radiation as one system)

Changing from the independent variable  $\xi_0$  to  $x$ , Eddington's fundamental differential equation<sup>6</sup> for small adiabatic oscillations of amplitude  $\xi_1$  reduces to

$$\xi_1'' + \frac{4-\nu}{x} \xi_1' + \frac{R \rho_0}{P_0} \left( \frac{n^2 R}{\gamma} - \frac{\alpha g_0}{x} \right) \xi_1 = 0, \quad (2)$$

where the dashes denote differentiation with respect to  $x$

With the substitutions (1), the differential equation (2) becomes in the limit

$$(1-x^3) \xi_1'' + \frac{1-4x^3}{x} \xi_1' + \left( f x - \frac{3\alpha}{x^2} \right) \xi_1 = 0, \quad (3)$$

where

$$f = \frac{9n^2}{4\pi G \gamma \rho} \quad (3')$$

Equation (3) has regular singularities<sup>16</sup> at  $x=0$  and at  $x=1$ . The roots of the indicial equation<sup>16</sup> are  $\pm \sqrt{3}\alpha$ . Assume

$$\xi_1 = x^q \sum_{\lambda=0}^{\infty} b_{\lambda} x^{\lambda} \quad (4)$$

as a series solution of (3),  
where

$$q = \pm \sqrt{3}\alpha, \quad (4')$$

and we leave  $b_0$  arbitrary for the present

Substituting (4) in (3) we find that all coefficients vanish except those which are multiples of 3, and that these obey the recurrence formula

$$b_{\lambda+3} = \frac{(\lambda+q)(\lambda+q+3)-f}{(\lambda+q+3)^2-3\alpha} b_{\lambda}, \quad (5)$$

where  $\lambda$  is a multiple of 3, say  $\lambda=3j$ , where  $j$  is integral or 0

We have from (5) that the series solution (4) terminates when

$$f=(3j+q)(3j+q+3) \quad (6)$$

Otherwise, (4) is an infinite series which can easily be shown to be convergent for  $x < 1$  but divergent for  $x=1$  (that is, on the surface of the model). In this case we shall have, by the extension of Abel's theorem<sup>4</sup> to series divergent on the circle of convergence, the limit of the amplitude infinite on the surface.

Hence, the modes of small radial oscillation are given by (6), where  $j$  is a positive integer or zero. The value  $j=0$  gives the fundamental mode.

The atmosphere being of infinitesimal density exerts no appreciable pressure on the nucleus. Hence, the nucleus oscillates as though the atmosphere were non-existent. The modes of small oscillation for the homogeneous sphere have been obtained by Sterne<sup>1,2</sup>. If  $\rho'$  be the density, the gravity and pressure will respectively be given by

$$g_0 = \frac{4\pi}{3} G \xi_0 \rho', \text{ and } P_0 = \frac{2\pi}{3} G \rho'^2 (R^2 - \xi_0^2)$$

In this case,

$$\nu = \frac{2x^2}{1-x^2}$$

With these substitutions, equation (2) reduces to

$$(1-\tau^2)\xi_1'' + \frac{4-6x^2}{x} \xi_1' + J\xi_1 = 0, \quad (7)$$

where

$$J = \frac{3n^2}{2\pi G \rho' \gamma} - 2\alpha \quad (8)$$

Reasoning as in (3), Sterne<sup>1,2</sup> finds the modes to be given by

$$J = 2j'(2j'+5), \quad (9)$$

where  $j'$  is integral or zero. The fundamental mode is given by  $j'=0$ .

For the generalised Roche's model, the periods given by (6) and (9) should agree. Eliminating  $n$  between (6) and (9), we have

$$\frac{(3j+q)(3j+q+3)}{2j'(2j'+5)+2\alpha} = \frac{\rho'}{\rho} \quad . \quad . \quad . \quad (10)$$

As the whole mass of the sphere ultimately condenses into the nucleus, we have

$$\dagger \pi R^3 \rho = \dagger \pi a^3 \rho',$$

whence we have

$$\bar{\rho}'/\bar{\rho} = R^3/a^3 \quad (11)$$

Substituting (11) in (10), we have

$$\frac{a^3}{R^3} = \frac{3j'(2j'+5)+3\alpha}{(j+q)(3j+q+3)} \quad (12)$$

We see from equation (12) that the volume of the nucleus cannot be arbitrary in the generalised Roche's model. In order to give a well-defined period of radial oscillation, the ratio  $a/R$  must satisfy equation (12), where  $j$  and  $j'$  are integral (including the value zero), and  $q$  is given by (4')

Further, the amplitude of the oscillations must agree on the surface of separation. The values for the first three modes of oscillation of the homogeneous sphere are, as given by Sterne,<sup>1,2</sup>

$$\left. \begin{aligned} j' &= 0, & \xi_1 &= 1, \\ j' &= 1, & \xi_1 &= 1 - \frac{1}{2}x^2, \\ \text{and } j' &= 2, & \xi_1 &= 1 - \frac{18}{5}x^2 + \frac{99}{35}x^4 \end{aligned} \right\} \quad (13)$$

From (5), we obtain the following corresponding values of the amplitude for the annulus

$$\left. \begin{aligned} j &= 0, & \xi_1 &= b_0 x^q, \\ j &= 1, & \xi_1 &= b_0 x^q - 6 \frac{q+3}{(q+3)^2 - 3\alpha} b_0 x^{q+2}, \\ \text{and } j &= 2, & \xi_1 &= b_0 x^q - 6 \frac{2q+9}{(q+3)^2 - 3\alpha} b_0 x^{q+2} + 36 \frac{(q+6)(2q+9)b_0 x^{q+4}}{\{(q+3)^2 - 3\alpha\}\{(q+6)^2 - 3\alpha\}} \end{aligned} \right\} \quad (14)$$

In view of the importance of the fundamental mode of oscillation, we will work out this case in detail.

For the fundamental modes of oscillation of nucleus and annulus, we have  $j=j'=0$ , and we have from (12)

$$\frac{a^3}{R^3} = \frac{\alpha}{\alpha + \sqrt{3\alpha}} \quad (15)$$

We do not consider the value  $q = -\sqrt{3\alpha}$ , as it will give a negative value for  $a/R$ .

We have from (12),  $\xi_1 = 1$ , and from (14),  $\xi_1 = b_0 x^2$ . In order that these may agree on the interface, we choose  $b_0 = (a/R)^{-2}$ , where  $a/R$  is given by (15). Thus  $b_0$  is no longer arbitrary.

The ratio  $a/R$  given by (15) depends on the value of  $\alpha$  which lies<sup>1,2</sup> between 0 and 6. We cannot have  $\alpha=0$ , as then  $n=0$ , and the period becomes infinite. We very well know that the value  $\alpha=0$  or  $\gamma=4/3$  separates the regions of stability and instability for radial oscillations<sup>6</sup>. Below we tabulate, for different values of  $\alpha$ , the values of the ratios  $a/R$  and  $a^3/R^3$ , that is, the ratios between the radii and volumes, respectively, of the nucleus and the whole sphere.

$\alpha$	1	2	3	4	5	6
$a/R$	53	59	62	65	66	68
$a^3/R^3$	15	21	24	27	29	31

Thus we see that the nucleus can at the most occupy about 30% of the volume of the whole sphere. For actual stars,  $\alpha$  lies between<sup>7</sup> 4 and 6, and for these values of  $\alpha$  the nucleus will have about 25 to 30 per cent of the total volume.

We have established agreement between the fundamental modes of oscillation of the nucleus and the annulus by choosing a particular value for the ratio  $a/R$ . It is evident that, on putting this value of  $a/R$  in (12), it will not in general be possible to get a pair of integral values,  $j$  and  $j'$ , (other than both zeros), satisfying (12), and that, even if it were possible to get such a pair, the pair thus obtained would hardly give the same value of  $\xi_1$  in (13) as in (14) when  $x =$  the chosen value for  $a/R$ . Thus there would not be agreement between the higher modes, when the fundamental modes of oscillation of the nucleus and annulus agree.

A similar argument to that given above would show that the generalised Roche's model can vibrate in only one mode.

We will now consider the large radial oscillations of the generalised Roche's model. The instability of large radial oscillations for the homogeneous sphere has been shown by A. C. Banerji in connection with his very interesting and entirely novel Cepheid theory<sup>1</sup> of the origin of the solar system. The nucleus, which is homogeneous, will therefore be unstable for large radial oscillations. We will consider the annulus.

The fundamental differential equations for large radial oscillations have been obtained by Banerji<sup>1</sup> and Bhatnagar<sup>\*</sup>. It has been assumed that

$$\xi_1 = a_1 \cos nt - a_2 \cos 2nt - a_3,$$

where  $a_1$  is a small quantity of the first order, and  $a_2$  and  $a_3$  are small quantities

<sup>\*</sup> Unpublished thesis for Ph. D. of A. U.

of the second order in  $\xi_1$  (the amplitude) Neglecting small quantities of the third and higher orders, the equations obtained are

$$a_1'' + \frac{4-\gamma}{\xi_0} a_1' + \left[ \frac{n^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] a_1 = 0, \quad (16)$$

$$a_2'' + \frac{4-\gamma}{\xi_0} a_2' + \left[ \frac{4n^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] a_2 = Q \quad (17)$$

and 
$$a_3'' + \frac{4-\gamma}{\xi_0} a_3' - \frac{\alpha \nu}{\xi_0^2} a_3 = Q, \quad (18)$$

where 
$$\nu = \frac{q_0 \rho_0 \xi_0}{P_0}, \quad \alpha = 3 - \frac{4}{\gamma} \quad (19)$$

and 
$$Q = \left[ \frac{1}{2}(3\gamma-1) \frac{n^2 \rho_0}{P_0 \gamma} - \frac{3}{4}(\gamma-1) \frac{\alpha \nu}{\xi_0^2} \right] a_1^2 + \frac{1}{2}(\gamma+1) \left[ \frac{n^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] \xi_0 a_1 a_1' + \left[ 1 - \frac{1}{2}(\gamma+1)\nu \right] a_1'^2 \quad (20)$$

and the dashes denote differentiation with respect to  $\xi_0$

With the substitutions (1), the differential equations (16), (17) and (18) become, in the limit,

$$(1-x^2) \frac{d^2 a_1}{dx^2} + \frac{1-4x^2}{x} \frac{da_1}{dx} + (fx^2 - 3\alpha) \frac{a_1}{x} = 0 \quad (21)$$

$$(1-x^2) \frac{d^2 a_2}{dx^2} + \frac{1-4x^2}{x} \frac{da_2}{dx} + (4fx^2 - 3\alpha) \frac{a_2}{x} = P \quad (22)$$

and 
$$(1-x^2) \frac{d^2 a_3}{dx^2} + \frac{1-4x^2}{x} \frac{da_3}{dx} - \frac{3}{\gamma} \frac{a_3}{x} = P, \quad (23)$$

where 
$$P = \left[ \frac{1}{2}(3\gamma-1) fx^2 - \frac{9}{4} \alpha(\gamma-1) \right] \frac{a_1^2}{x^2} + \frac{1}{2}(\gamma+1) (fx^2 - 3\alpha) \frac{a_1}{x} \frac{da_1}{dx} + \left[ \frac{1}{2}(1-3\gamma) - x^2 \right] \left( \frac{da_1}{dx} \right)^2 \quad (24)$$

and 
$$f = 9n^2/(4\pi G\gamma\rho) \quad (25)$$

Assume the following series solution for (21)

$$a_1 = x^2 \sum_{\lambda} b_{\lambda} x^{\lambda} \quad (26)$$

The roots of the indicial equation are

$$q = \pm \sqrt{3\alpha} \quad (27)$$

Substituting (26) in (21), we find that the only non-vanishing co-efficients are those for which

$$\lambda = 3j, \quad . \quad . \quad . \quad (28)$$

where  $j$  is zero or a positive integer, and that the co-efficients obey the recurrence formula

$$b_{\lambda+3} = \frac{(\lambda+q)(\lambda+q+3)-f}{(\lambda+q+3)^2-3\alpha} b_{\lambda} \quad (29)$$

When

$$f = (\lambda+q)(\lambda+q+3), \quad (30)$$

the series (26) terminates, otherwise, (26) is an infinite series, which can be shown to be convergent for  $x < 1$  but divergent when  $x = 1$  (that is, on the boundary). Hence, by the extension of Abel's theorem<sup>4</sup>,  $f$  must satisfy (30) in order that modes of radial oscillation may be possible.

Suppose that the equation (30) is satisfied and the series (26) for  $a_1$  terminates.

Let the complementary function for (22) be

$$a_2 = x^q \sum_0^{\infty} c_{\lambda} x^{\lambda}, \quad (31)$$

We find that the indicial equation gives the same roots as in (27), and the recurrence formula for the co-efficients is

$$c_{\lambda+3} = \frac{(\lambda+q)(\lambda+q+3)-4f}{(\lambda+q+3)^2-3\alpha} c_{\lambda}, \quad . \quad . \quad (32)$$

where  $\lambda$  is of the form in (28).

As  $a_1$  is a terminating series in  $x$ , so is  $P$  by (24). Hence the co-efficients of the particular integral of (22) will ultimately satisfy the same recurrence formula as (32).

As before, we find that for the modes of radial oscillation to be possible, the series (31) for  $a_2$  must also terminate, that is, we must have

$$4f = (\lambda+q)(\lambda+q+3). \quad (33)$$

Let us suppose that (30) and (33) are simultaneously satisfied and that the series for  $a_1$  and  $a_2$  both terminate.

The complementary function of (23) is

$$a_3 = x^q \sum_0^{\infty} d_{\lambda} x^{\lambda}, \quad . \quad . \quad (34)$$



where the indicial equation gives the same roots as in (27), and the recurrence formula for the co-efficients is

$$d_{\lambda+3} = \frac{(\lambda+q)(\lambda+q+3)}{(\lambda+q+3)^2 - \frac{3}{\gamma}} d_{\lambda}, \quad . \quad . \quad . \quad (35)$$

where  $\lambda$  is of the form in (28)

As before, it can be shown that for the radial oscillations to be possible, we must have

$$(\lambda+q)(\lambda+q+3)=0 \quad . \quad . \quad . \quad (36)$$

Hence, we have that the equations (30), (33) and (36) must be simultaneously satisfied in order that modes of radial oscillation may be possible. From (27), we have the following two cases.

CASE (a)  $q = \sqrt{3}\alpha$

It is evident that (30), (33) and (36) are simultaneously satisfied when  $\lambda = q = f = 0$ . In that case, we have from (25) that  $n=0$ , or the period is infinite, which means that the sphere is in neutral equilibrium. This is also evident from the fact that when  $q=0$  then  $\alpha=0$  and  $\gamma=4/3$ , from (19). We know that the value  $\gamma=4/3$  is where the transition from stability to instability sets in for radial oscillations.\*

As we can have only the positive root in (27) for the Roche's model, we obtain, as a particular case, Bhatnagar's result\* that the Roche's model cannot execute large radial oscillations.

CASE (b),  $q = -\sqrt{3}\alpha$ .

As  $\alpha$  lies<sup>12</sup> between 0 and 6, in this case one possibility is as in Case (a) above, which has already been discussed. The other is  $\lambda = -q = 1$  in (36). In this case we have, if (30) and (33) are to be simultaneously satisfied,

$$(\lambda-1)(\lambda+2) = 4(\lambda'-1)(\lambda'+2) \quad (37)$$

for integral pairs of values of  $\lambda$  and  $\lambda'$ .

From (37), we have

$$\lambda' = \frac{-1 \pm \sqrt{\lambda^2 + \lambda + 7}}{2} \quad . \quad (38)$$

We have from (28) that both  $\lambda$  and  $\lambda'$  in (38) must be multiples of 3. We find that amongst the lower modes this condition is only satisfied by the pair  $\lambda=6, \lambda'=3$ .

$\lambda'=3$  means  $j=1$  in (12), that is, the first mode in the annulus. Putting  $j=1, q=-1$  in (12), we have

$$\frac{\alpha^3}{R^3} = \frac{3j'(2j'+5)+1}{10}, \quad . \quad . \quad . \quad (39)$$

as

$$\alpha = q^3/3 = 1/3.$$

\* Unpublished thesis for Ph.D. of A. U.

(39) is only possible when  $f=0$ , and in this case we have

$$\frac{a^2}{R^2}=1, \text{ whence we have } \frac{a}{R} = 46 \quad . \quad . \quad (40)$$

Thus amongst the lower modes the only possible combination for large radial oscillations of the generalised Roche's model is the fundamental mode of the nucleus and the first mode of the annulus, and the ratio of the radii of the nucleus and the model must satisfy (40)

The sharp value of  $\gamma$  that we get, viz., 1.5, shows that the model will be unstable for large radial oscillations if the actual value of  $\gamma$  differs appreciably from the theoretical value (1.5)

The homogeneous nucleus in any case cannot execute large radial oscillations, as shown by Banerji,<sup>3</sup> and therefore the generalised Roche's model is incapable of large radial oscillations

This enables us to draw a tentative picture of the origin of the spiral nebulae. We imagine a nebula of the form of the generalised Roche's model, oscillating with small amplitude. A catastrophe, such as explosions of stars in the nucleus, increases the amplitude of the oscillations, so that instability ensues and matter is ejected in the equatorial plane,<sup>11</sup> which forms the spiral arms. This possibility in the case of the Roche's model has been indicated by Bhatnagar.\*

The author considers it a great privilege to record his sincere thanks to Professor A. C. Banerji, under whose guidance he has carried out the above investigation.

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# CHEMICAL EXAMINATION OF THE SEEDS OF *NIGELLA SATIVA*, LINN. (MAGREL) PART II THE COMPONENT GLYCERIDES OF THE FATTY OIL

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## SUMMARY

The component glycerides of the oil of *Nigella sativa* have been examined. The percentages of oleic, linoleic and solid acids have been calculated from the thiocyanogen value and these results have been found to be in fair agreement with those reported previously in Part I. The component glycerides of the oil in round figures are as follows —

Trilinolein 2%, oleodilinolein 25%, dioleolinolein 42%, palmitooleolinolein 24%, and stearooleolinolein 7%. The palmitoglyceride contains small amounts of myristic acid.

In a previous communication<sup>1</sup> the authors examined the component acids of the fatty oil, from the seeds of *Nigella sativa*. In the present investigation the percentages of oleic, linoleic and solid acids have been confirmed by the determination of the thiocyanogen value and also the component glycerides of the oil have been examined by brominating the neutral oil in petroleum ether (B.P. 40°–60°C) at –5°C and resolving the brominated product into a number of fractions<sup>2, 3</sup>. No solid was obtained by chilling the oil in acetone showing the absence of fully saturated and disaturated glycerides. The absence of fully saturated glycerides was further confirmed by oxidising the oil with potassium permanganate in acetone solution according to the method of Hilditch and Lea<sup>4</sup> when no neutral product was obtained.

The component acids of the oil determined by this method are in fair agreement with those reported in Part I. The comparison is shown in Table 3.

The component glycerides of the oil in round figures are as follows (Table 4). — Trilinolein 2%; oleodilinolein 25%, dioleolinolein 42%, palmitooleolinolein 24% and stearooleolinolein 7%. The palmitoglyceride contains small amount of myristic acid. Our experiments have thus shown the actual number of chief glycerides to be five, whereas the maximum number of individual glycerides, which may be obtained by

any permutation of the four main acids, in combination with the trihydric glyceryl radical  $\text{CH}_2-\underset{|}{\text{CH}}-\underset{|}{\text{CH}_2}$ , is 40

### EXPERIMENTAL

The thiocyanogen values of the oil and of the mixed fatty acids were determined and found to be 81.20 and 82.22 respectively. The percentages of the oleic, linoleic and solid acids in mixed acids were then calculated from the thiocyanogen value (82.22) and the iodine value (119.10) of the mixed fatty acids. They are as follows

Acids	Percentage in mixed acids
Oleic	50.43 (49.67)
Linoleic	40.70 (40.22)
Solid (saturated)	8.87 (10.11)

These results are in fair agreement with those obtained by Twitchell's lead salt-alcohol process and bromination of the liquid acids, which are also given above in brackets for comparison.

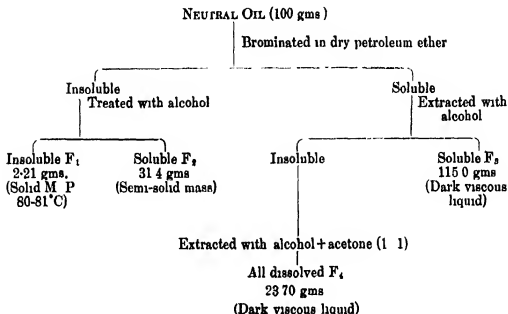
The oil was then made neutral by treating with sodium carbonate and purified with animal charcoal and Fuller's earth.

The neutral oil (118.2 gms) was dissolved in six times its weight of dry acetone and kept in a frigidare for about six days. No solid separated showing the absence of any fully saturated or disaturated glycerides.

The absence of fully saturated glycerides was further confirmed by oxidising 101.8 gms. of the neutral oil in ten times its weight of acetone with 410 gms. of powdered potassium permanganate according to the method of Hilditch and Lea (*loc. cit.*). The process was repeated two times when ultimately no neutral substance was obtained.

One hundred grams of the neutral oil was then dissolved in a litre of dry petroleum ether (B.P. 40°–60°C), cooled to –5°C and bromine added till it was in slight excess which was indicated by the colour of the solution turning to permanently brown. This was kept overnight in a frigidare when some solid mass separated. This was filtered off and washed with chilled petroleum ether. The solid mass left on the filter paper was resolved into two fractions  $F_1$  and  $F_2$  by crystallising from absolute alcohol. The petroleum ether filtrate was treated with a solution of sodium thiosulphate to remove excess of bromine, washed with water, dried over fused calcium chloride and the solvent was distilled off when a dark viscous liquid was left. This was extracted with alcohol. The alcohol insoluble portion was then treated with a mixture of alcohol and

acetone (1 : 1) when the whole of it dissolved. The scheme of separation is shown below —



The fractions F<sub>1</sub>, F<sub>3</sub> and F<sub>4</sub> were then debrominated by taking them in methyl alcohol, adding zinc dust, saturating the solution with dry hydrochloric acid gas and then refluxing for several hours. The debrominated products were then saponified with alcoholic potassium hydroxide, the unsaponifiable matter removed with ether and the fatty acids liberated with dilute sulphuric acid. The saponification equivalent, the iodine value and the thiocyanogen value of the liberated acids from all the three fractions were then determined and from these the quantities of individual acids were calculated. The amount of saturated acids being too small for estimating them separately they were considered as one acid. The fractions containing solid acids were then oxidised with potassium permanganate in alkaline solution according to the method of Lapworth and Mottram,<sup>6</sup> the oxidation product extracted with petroleum ether and the saponification equivalents of the acids so obtained were determined.

The amount of F<sub>1</sub> being too small, it was not subjected to debromination and other subsequent operations. Its bromine contents were determined by the Piria and Schiff's method. This was found to be a triglyceride of tetrabromo linoleic acid. (Found Br = 52.039%, C<sub>57</sub>, H<sub>88</sub>, O<sub>6</sub>, Br<sub>12</sub>; requires Br = 52.26 %).

The results of bromination and analysis are given below in Tables I, II and III.

TABLE I

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>
Weight in grams	2 2152	31 10	115 00	23 70
Wt. of the debrominated product (glyceride + unsaponifiable)	1 0868	16 37	68 87	13 59
Wt. of the unsaponifiable matter		0 009	0 02	
Wt. percentage of glycerides (free from unsaponifiable)	1 09	16 38	68 93	13 60
Saponification equivalent of liberated acids		280 30	280 50	280 30
Iodine value		152 33	111 18	123 35
Thiocyanogen value		90 42	78 77	82 31
Saponification equivalent of saturated acids			264 81	282 10

TABLE II

	Mol per cent of acids in each fraction			
	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>
	1 09%	16 39%	68 92%	13 60%
Lanoleic acid	100	68 45	35 65	45 46
Oleic acid		31 55	50 99	45 74
Saturated acids			13 36	8 80

TABLE III

	Mol. per cent. of acids on total acids				
	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	Mean
Lanoleic	1 09	11 22	24 57	6 19	43 07 (40 19)
Oleic		5 17	35 14	6 22	46 53 (49 29)
Saturated			9 21	1 19	10 40 (10 52)

These results are in fair agreement with those obtained for the component fatty acids of the oil as reported in Part I<sup>1</sup>. Their mol. per cent are given in brackets for comparison.

From the above figures the component glycerides of the oil of *Nigella sativa* have been calculated as shown below in Table IV.

TABLE IV

Estimated Component Glycerides of the Oil of *Nigella sativa* (mol per cent)

Glycerides in		F <sub>1</sub>	I <sub>2</sub>	I <sub>3</sub>	F <sub>4</sub>	Mean
		1 09	16 39	68 97	13 60	100
1	Fully saturated glycerides	nil	nil	nil	nil	
2	Disaturated glycerides	nil	nil	nil	nil	
3	Monosaturated diunsaturated glycerides					
	(a) Monosaturated oleolinolein			7 63	3 77	31 90
4	Triunsaturated glycerides					
	(a) Trilinolein	1 01	0 88			1 97
	(b) Oleodilinolein		15 51	4 71	4 37	25 97
	(c) Dioleolinolein			36 50	7 06	41 56

In the above calculations all the saturated acids have been considered as one acid. According to the law of even distribution there are greater possibilities for the presence of glycerides with all the three different acids than with only two different acids, hence we are justified to assume that the saturated acids in F<sub>3</sub> and F<sub>4</sub> are combined as saturated oleolinolein rather than as saturated dilinolein or as saturated diolein. Also as all the saturated acids of the oil of *Nigella sativa* are combined as monosaturated diunsaturated glycerides we can assume that they are proportionally divided in saturated oleolinolein. From the above considerations the component glycerides of the oil of *Nigella sativa* may be given in round figures as follows — Trilinolein 2% oleodilinolein 25% dioleolinolein 42% palmitooleolinolein 24% and stearooleolinolein 7%. The palmito glyceride will contain small amounts of myristic acid as in the above calculations the amount of myristic acid being too small (less than 1%) it has been included in palmitic acid.

## ACKNOWLEDGEMENTS

We wish to make grateful acknowledgement to the Kanta Prasad Research Scholarship Endowment Trust of the United Provinces for the award of a research scholarship to one of us (Ram Das Tewari) which has enabled him to take part in this investigation and also to the University of Allahabad for research facilities.

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STUDIES ON THE NATURE OF RACEMIC MODIFICATIONS OF  
OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE. PART I-  
ANILINE, *o*-, *m*- AND *p*-TOLUIDINE,  $\alpha$ -NAPHTHYLAMINE,  $\beta$ -  
NAPHTHYLAMINE, AND *a*-TETRAHYDRO- $\alpha$ -NAPHTHYL-  
AMINE SALTS OF CAMPHOR- $\beta$ -SULPHONIC ACIDS

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In previous studies<sup>1</sup> of enantiomorphs and then racemic modifications by one of us, the question of the nature of the racemic modification has never been thoroughly investigated. In this paper we have undertaken the study of the nature of the racemic forms of salts of *d*-, *l*-, and *dl*-camphor- $\beta$ -sulphonic acids with aniline, *o*-, *m*-, *p*-toluidine,  $\alpha$ -naphthylamine,  $\beta$ -naphthylamine, and *a*-tetrahydro- $\alpha$ -naphthylamine.

According to Pasteur's principle of Molecular Dissymmetry, the *d*- and *l*-forms must possess the same total energy. They must also possess the same scalar properties such as density, viscosity, crystal lustre, solubility, etc. But they must differ in such vectorial physical properties, as for example, the direction of rotation of the plane of polarisation of light, unsymmetrical distribution of hemihedral facets in the crystal forms in which these facets are developed,\* and also in the enantiomorphous distribution of pyro- and piezo-electrical polarity. The magnitude of these vectorial properties is, however, identical for the enantiomorphous forms.

The enantiomorphous modifications may occur in equimolecular proportions to constitute what is known as a racemic form. The properties of the racemic modification will vary according to whether it is (i) a mixture of the two optically active and opposite forms in equal proportions, (*d*- and *l*-), or (ii) a compound of these two forms, (*dl*-), or (iii) a solid solution of the dextro and laevo forms due to the enantiomorphs being isomorphous, each crystal containing both the forms. The last case differs from the first in constituting a single phase unlike in a mixture.

Roozeboom<sup>2</sup> has devised two methods for distinguishing between the above-mentioned types of racemic modifications. The first of these methods is the *Freezing-point Method*. It is possible to determine the nature of the racemic

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\* Contrary to Pasteur's dictum that hemihedry was invariably associated with molecular dissymmetry, subsequent work has shown that this does not hold in all cases. (Frankland, Pasteur Memorial Lecture, *Jour Chem Soc*, 1897, 71, 692)



modification from the melting-point determinations\* A racemic modification may melt at the same temperature as the optically active forms or at higher or lower temperatures If the melting-point of the racemic form is higher than or equal to that of the active forms, it is a true racemic compound But if it is lower, then the nature of the racemic form cannot be decided without making a melting-point-composition curve We may, therefore, discuss the types of melting point-composition curves that can be obtained from mixtures of racemic modification and *d*- and *l*-components

Type I—Melting-point-composition curve of racemic mixture and its *d*- or *l*-modification

In this case the racemic form is the eutectic mixture of *d*- and *l*-components in equal proportions The melting-point-composition diagram will consist of two symmetrical curves as shown in Fig I as none of the compounds investigated here are racemic mixtures, a racemic mixture was prepared by mixing equal quantities of salts of  $\beta$ -naphthylamine with *d*- and *l*-camphor- $\beta$ -sulphonic acid One such case,<sup>5</sup> namely, the racemic modification of *p*-phenylene-bisimino-camphor, which was found by this method to be a racemic mixture, has already been reported by one of us

Type II—Melting-point-composition curves of racemic compound and its *d*- or *l*-modification

Three kinds of curves are possible under this type, *viz*, (a) where the racemic form has a melting-point lower than that of the enantiomorphs (Figs 2–6), (b) where the racemic form has a higher melting-point (Fig 7), and (c) where the racemic form has the same melting point as the enantiomorphs (Fig 8) In this case, unlike, in Type I, there will be two eutectic points, symmetrically placed, giving rise to three distinct curves—Figs 2, 3, 4, 5 and 6, correspond to aniline-camphor- $\beta$ -sulphonates, *o*-toluidine-camphor- $\beta$ -sulphonates, *m*-toluidine-camphor- $\beta$ -sulphonates, *p*-toluidine-camphor- $\beta$ -sulphonates and  $\alpha$ -naphthylamine-camphor- $\beta$ -sulphonates respectively, and Fig 7 to  $\beta$ -naphthylamine-camphor- $\beta$ -sulphonates, and Fig 8 to *ar*-tetrahydro- $\alpha$ -naphthylamine-camphor- $\beta$ -sulphonates.

Type III—In the case where the racemic form is a solid solution, its melting-point may be the same as that of the optically active components, or it may be higher or lower, but the melting-point-composition diagram will be a single curve

A study of the curves referring to Types I and II indicates a convenient and quick method for determining whether the racemic modification is a compound or a mixture, a small amount (less than that required for the eutectic mixture) of the

\* This will not characterise racemic solid solutions It will be necessary to prepare a melting-point-composition diagram of the mixture of the racemic modification and the optical enantiomorphs. If a single curve is obtained then we are dealing with a racemic solid solution

*d*- or *l*-form is added to the racemic modification, if the melting-point is raised it is a mixture, and if, on the other hand, it is lowered then it is a compound

There is a second method (due also to Roozeboom<sup>2</sup> and Bruni<sup>4</sup>) derived from phase rule depending on the solubility relationships existing between the optical isomers and their racemic mixtures, compounds or solid solutions. The solubility-composition isotherms, which they have derived theoretically, have not yet been established experimentally. The reasoning is as follows—the addition of a solid fusible phase lowers the melting-point of an organic compound, similarly, a second soluble phase alters its solubility. Hence if a solubility-composition isotherm of a racemic modification with its dextro and lævo isomers is plotted, a racemic mixture should give two curves, a racemic solid solution one curve and a racemic compound three curves. We propose to undertake this experimental study as soon as sufficient amount of materials have been prepared.

### EXPERIMENTAL

The salts of the organic bases with *d*-camphor- $\beta$ -sulphonic acid have been found, on heating to a high temperature, to lose a molecule of water with the formation of the corresponding anils<sup>6</sup>. In order to overcome this difficulty, the melting points were determined instead of the freezing-points as the latter process involves heating the compound above its melting point for a considerable time. An intimate mixture of accurately weighed quantities of the racemic modification with *d*- or *l*-form was made and the melting-points were determined by the capillary tube method. The results are given in Tables I to VIII.

$\beta$ -naphthylamine-camphor- $\beta$ -sulphonates<sup>7</sup>. The racemic modification, prepared from  $\beta$ -naphthylamine and *dl*-camphor- $\beta$ -sulphonic acid, melts at 183.5°C. As is evident from Fig. 7, it is a racemic compound and it corresponds to Type II. The melting point determinations are given in Table VII.

As in none of the cases reported here we have come across a true racemic mixture by synthesis, a racemic mixture of the substance was prepared by mixing equal weights of the *d*- and *l*-isomers. This eutectic mixture melts at 161.5°C which is the lowest melting-point of all the mixtures (*vide* Table I) and, therefore, conforms to Type I (Fig. 1) discussed above. When this racemic mixture was dissolved in water and the solution allowed to evaporate spontaneously in vacuum at room temperature (30.0°C) it yielded the above-mentioned racemic mixture melting at 161.5°C, indicating that the transition temperature of the system is above 30.0°C.

\* This salt and the subsequent ones described here are new compounds and will be treated in detail in a later communication. The aniline salt of *d*-camphor- $\beta$ -sulphonic acid has, however, been reported by Schreiber and Shrinet.<sup>8</sup>

**Aniline-camphor- $\beta$ -sulphonates** The racemic modification as prepared from aniline and *dl*-camphor- $\beta$ -sulphonic acid melts at 170.0°C. As is evident from Fig. 2, it is a racemic compound and it conforms to Type II. The melting-point determinations are given in Table II.

***o*-Toluidine-camphor- $\beta$ -sulphonates** The racemic modification as prepared from *o*-toluidine and *dl*-camphor- $\beta$ -sulphonic acid melts at 144.0°. It is evident from Fig. 3 that it is a racemic compound and it corresponds to Type II. The melting-point determinations are given in Table III.

***m*-Toluidine-camphor- $\beta$ -sulphonates** The racemic modification as prepared from *m*-toluidine and *dl*-camphor- $\beta$ -sulphonic acid melts at 145.0°C. As is evident from Fig. 4 it is a racemic compound and conforms to Type II. The melting-point determinations are given in Table IV.

***p*-Toluidine-camphor- $\beta$ -sulphonates** The racemic modification, as prepared from *p*-toluidine and *dl*-camphor- $\beta$ -sulphonic acid, melts at 155.0°C. It is evident from Fig. 5 that it is a racemic compound conforming to Type II. The melting-point determinations are given in Table V.

**$\alpha$ -Naphthylamine-camphor- $\beta$ -sulphonates** The racemic modification as prepared from  $\alpha$ -naphthylamine and *dl*-camphor- $\beta$ -sulphonic acid melts at 165.0°C. As is evident from Fig. 6 it is a racemic compound and it is of Type II. The melting-point determinations are given in Table VI.

***ar*-Tetrahydro- $\alpha$ -naphthylamine-camphor- $\beta$ -sulphonates** The racemic modification as prepared from *ar*-tetrahydro- $\alpha$ -naphthylamine and *dl*-camphor-sulphonic acid melts at 163.0°C. It is evident from Fig. 8, that it is a racemic compound of Type II. The melting point determinations are given in Table VIII.

TABLE I

 $\beta$ -Naphthylamine-camphor- $\beta$ -sulphonates

Mixed melting-points of the racemic modifications, Type I (mixture), with *l*- and *d*-isomers

Wt. % of <i>l</i> - or <i>d</i> -component.	Wt. % of the racemic mixture.	Melting-point of the mixture.
0	100	161.5°C
20 <i>l</i> -	80	162.5°C
40 "	60	163.0°C
60 "	40	164.0°C
80 "	20	164.5°C
100 "	0	165.5°C
20 <i>d</i> -	80	162.0°C
40 "	60	163.0°C
60 "	40	164.5°C
80 "	20	165.0°C
100 "	0	165.5°C

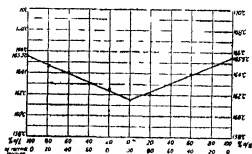


Fig. 1  
 $\beta$ -Naphthylamine-camphor- $\beta$ -sulphonates

TABLE II  
Aniline-camphor- $\beta$ -sulphonates

Mixed melting-points of the racemic modification, Type II (compound),  
with *l*- and *d*-isomers

Wt. % of <i>l</i> - or <i>d</i> - component	Wt. % of racemic compound,	Melting-point of the mixture
0	100	170.0°C
10 <i>l</i> -	90	169.6°C
20 "	80	169.0°C
30 "	70	167.4°C
40 "	60	169.8°C
50 "	50	172.0°C
60 "	40	174.4°C
70 "	30	176.6°C
80 "	20	179.0°C
90 "	10	181.2°C
100 "	0	183.5°C
10 <i>d</i> -	90	169.6°C
20 "	80	168.8°C
30 "	70	167.4°C
40 "	60	169.4°C
50 "	50	172.0°C
60 "	40	174.6°C
70 "	30	176.4°C
80 "	20	179.0°C
90 "	10	181.2°C
100 "	0	183.5°C

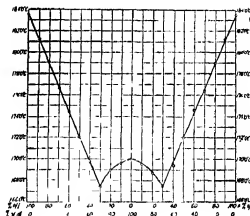


Fig. 2  
Aniline-camphor- $\beta$ -sulphonate

TABLE III  
*o*-Toluidine-camphor- $\beta$ -sulphonates

Mixed melting-points of the racemic modification, Type II (compound),  
with *l*- and *d*-isomers

Wt. % of <i>l</i> - or <i>d</i> - component	Wt. % of racemic compound	Melting-point of the mixture
0	100	144.0°C
10 <i>l</i> -	90	143.8°C
20 "	80	143.6°C
30 "	70	143.2°C
40 "	60	142.4°C
50 "	50	143.5°C
60 "	40	144.6°C
70 "	30	145.8°C
80 "	20	146.8°C
90 "	10	148.0°C
100 "	0	149.0°C

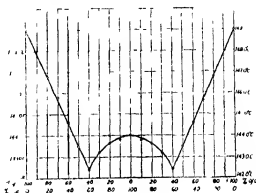


Fig. 3  
*o*-Toluidine-camphor- $\beta$ -sulphonates

Wt % of <i>l</i> - or <i>d</i> - component.	Wt % of racemic compound.	Melting-point of the mixture.
10 <i>d</i> -	90	143.8°C
20 "	80	143.6°C
30 "	70	143.2°C
40 "	60	142.4°C
50 "	50	143.5°C
60 "	40	144.6°C
70 "	30	145.6°C
80 "	20	146.8°C
90 "	10	147.8°C
100 "	0	149.0°C

TABLE IV

*m*-Toluidine-camphor- $\beta$ -sulphonatesMixed melting points of the racemic modification, Type II (compound),  
with *l*- and *d*-isomers.

Wt % of <i>l</i> - or <i>d</i> - component	Wt % of the racemic compound	Melting-point of the mixture
0	100	145.0°C
10 <i>l</i> -	90	144.8°C
20 "	80	144.6°C
30 "	70	144.2°C
40 "	60	143.8°C
50 "	50	144.6°C
60 "	40	145.4°C
70 "	30	146.2°C
80 "	20	147.2°C
90 "	10	148.2°C
100 "	0	149.0°C
10 <i>d</i> -	90	144.8°C
20 "	80	144.6°C
30 "	70	144.2°C
40 "	60	143.8°C
50 "	50	144.5°C
60 "	40	145.4°C
70 "	30	146.2°C
80 "	20	147.2°C
90 "	10	148.0°C
100 "	0	149.0°C

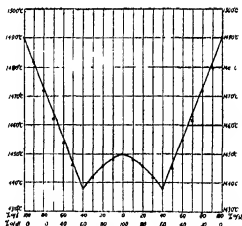


Fig. 4

*m*-Toluidine-camphor- $\beta$ -sulphonates

TABLE V

*p*-Toluidine-camphor- $\beta$ -sulphonatesMixed melting-points of the racemic modification, Type II (compound), with *l*- and *d*-isomers

Wt % of <i>l</i> - or <i>d</i> -component	Wt % of the racemic compound	Melting-point of the mixture
0	100	155.0°C
10 <i>l</i> -	90	154.5°C
20 "	80	153.0°C
30 "	70	152.0°C
40 "	60	154.0°C
50 "	50	157.0°C
60 "	40	159.0°C
70 "	30	161.5°C
80 "	20	165.5°C
90 "	10	168.0°C
100 "	0	170.0°C
10 <i>d</i> -	90	154.0°C
20 "	80	153.0°C
30 "	70	152.0°C
40 "	60	153.5°C
50 "	50	156.5°C
60 "	40	158.5°C
70 "	30	161.5°C
80 "	20	165.0°C
90 "	10	168.0°C
100 "	0	170.0°C

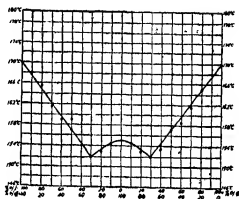


Fig 5

*p*-Toluidine-camphor- $\beta$ -sulphonates

TABLE VI

 $\alpha$ -Naphthylamine-camphor- $\beta$ -sulphonatesMixed melting points of the racemic modification, Type II (compound), with *l*- and *d*-isomers

Wt. % of <i>l</i> - or <i>d</i> -component	Wt % of the racemic compound	Melting-point of the mixture
0	100	165.0°C
10 <i>l</i> -	90	164.8°C
20 "	80	164.4°C
30 "	70	164.0°C
40 "	60	163.2°C
50 "	50	164.8°C
60 "	40	166.3°C
70 "	30	168.4°C
80 "	20	170.2°C
90 "	10	171.8°C
100 "	0	173.0°C

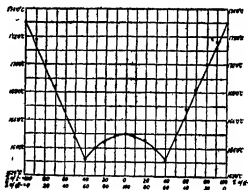


Fig 6

 $\alpha$ -Naphthylamine-camphor- $\beta$ -sulphonates

Wt % of <i>l</i> - or <i>d</i> - component	Wt % of the racemic compound	Melting-point of the mixture
10 <i>d</i> -	90	164.8°C
20 "	80	164.6°C
30 "	70	164.0°C
40 "	60	163.2°C
50 "	50	164.6°C
60 "	40	166.8°C
70 "	30	168.2°C
80 "	20	170.0°C
90 "	10	171.6°C
100 "	0	173.0°C

TABLE VII

 $\beta$ -Naphthylamine-camphor- $\beta$ -sulphonates

Mixed melting points of the racemic modification, Type II (compound), with  
*l*- and *d*-isomers

Wt % of <i>l</i> - or <i>d</i> - component.	Wt % of the racemic compound	Melting-point of the mixture.
0	100	183.5°C
10 <i>l</i> -	90	182.0°C
20 "	80	180.0°C
30 "	70	177.0°C
40 "	60	174.0°C
50 "	50	169.5°C
60 "	40	166.0°C
70 "	30	162.0°C
80 "	20	163.5°C
90 "	10	164.5°C
100 "	0	165.5°C
10 <i>d</i> -	90	182.0°C
20 "	80	180.0°C
30 "	70	177.0°C
40 "	60	173.5°C
50 "	50	169.5°C
60 "	40	166.5°C
70 "	30	162.0°C
80 "	20	163.5°C
90 "	10	164.5°C
100 "	0	165.5°C

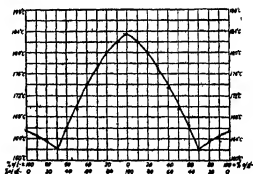


Fig. 7

$\beta$ -Naphthylamine-camphor- $\beta$ -  
sulphonates

TABLE VIII

*ar*-Tetrahydro- $\alpha$ -naphthylamine-camphor- $\beta$ -sulphonatesMixed melting points of the racemic modification Type II (compound) with *l*- and *d*-isomers

Wt. % of <i>l</i> - or <i>d</i> - component	Wt % of the racemic compound	Melting point of the mixture
0	100	163.0°C
10 <i>l</i> -	90	162.5°C
20 "	80	162.0°C
30 "	70	161.0°C
40 "	60	160.5°C
50 "	50	159.0°C
60 "	40	160.5°C
70 "	30	161.0°C
80 "	20	162.0°C
90 "	10	162.5°C
100 "	0	163.0°C
10 <i>d</i> -	90	162.5°C
20 "	80	162.0°C
30 "	70	161.5°C
40 "	60	160.5°C
50 "	50	159.0°C
60 "	40	160.5°C
70 "	30	161.0°C
80 "	20	162.0°C
90 "	10	162.5°C
100 "	0	163.0°C

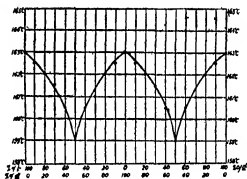


Fig 8

*ar*-Tetrahydro- $\alpha$ -naphthylamine-camphor- $\beta$ -sulphonates

Further work on this subject is in progress. We wish to make grateful acknowledgments to the Allahabad University for research facilities.

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PROCEEDINGS  
 OF THE  
 NATIONAL ACADEMY OF SCIENCES, INDIA  
 (SECTION A)

PART 2	MARCH, 1943	VOLUME 13
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THE CHEMICAL EXAMINATION OF THE FRUITS OF  
*TERMINALIA BELLERICA* ROXB PART I THE COM-  
 PONENT ACIDS OF THE FATTY OIL

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(Received — 21 December, 1942)

The kernels of the seeds of *Terminalia bellerica* Roxb on extraction with petroleum ether (40-60°C) yield 38.6% of a clear light yellow fatty oil having  $d_{40}^{20} 0.9108$ ,  $n_D^{20} 1.4601$ ,  $[\alpha]_D^{20} +0.04^\circ$  acid value 2.28, sap value 198.8, acetyl value 18.72, Hehner value 94.8, R.M. 0.82, iodine value (Hanus) 89.14, thiocyanogen value 65.0 and unsaponifiable matter (sitosterol M.P. 135°C) 0.53%.

The component fatty acids were found to be oleic (43.21%), linoleic (28.99%), palmitic (11.80%) and stearic (16.00%) acids.

*Terminalia bellerica*, Roxb commonly known as *Babeda* or *Bahera* in Hindi and Sanskrit and *bastard myrobalan* or *Baleric myrobalan* in English belongs to the Combretaceae family. It is commonly found in the forests of India, Burma and Ceylon upto a height of 3,000 feet. The fruit is nearly globular, suddenly narrowing into a short stalk,  $\frac{1}{2}$  to  $\frac{3}{4}$  inch in diameter. The stone is hard, pentagonal and contains a sweet oily kernel having three prominent ridges from the base to its apex.

According to Kirtikar and Basu,<sup>1</sup> Chopra,<sup>2</sup> Dey,<sup>3</sup> and Dymock<sup>4</sup>, the fruits of the plant are highly medicinal, nearly all the parts being used in various ailments. The fruit is an ingredient of the reputed Ayurvedic medicine *Triphala* (three fruits), the other two being *Har* (*Terminalia chebula*) and *Aonla* (*Phyllanthus embelica*). The fruit is bitter, pungent, acrid, digestible, laxative, anthelmintic and astringent. It is useful in dropsy, piles,

leprosy, diarrhoea, bronchitis, sore-throat, asthma and eye diseases. In combination with other drugs it is used in snake bite and scorpion sting. The kernel is popularly believed to be narcotic and intoxicant when taken internally and is useful in thirst, vomiting, bronchitis, eye troubles and urinary diseases. It is used with betel in dyspepsia and with honey in ophthalmia. The kernel oil is used as a dressing for hair and as a substitute for ghee by poorer classes of people in the Central Provinces. It relieves pain and swelling when rubbed in rheumatism and soothes the skin in burns.

In spite of the great medicinal value of the fruits very little work has been done on its chemical examination. A preliminary examination of the fruit is reported by Hooper<sup>5</sup> who showed the presence of tannic acid, gallo-tannic acid and a fatty oil, the characteristics of which are recorded and given in table I. Shrikhande and Godbole<sup>6</sup> examined the oil for its constants which are also given in table I. None of these workers have studied the component acids or the component glycerides of the fatty oil and the other constituents of the fruits. The present investigation was, therefore, undertaken and the component acids of the oil are reported in this paper. The component glycerides of the oil and other constituents of the fruits are under examination.

The constants of the oil as found by us (table I) are in fair agreement with those reported by Hooper (*loc. cit*), but differ slightly from those given by Shrikhande and Godbole (*loc. cit*).

The oil has been shown to consist of the glycerides of oleic, linoleic, palmitic and stearic acids together with a sitosterol (M.P. 135-136°C). The percentages of oleic and linoleic acids in mixed acids have also been calculated from the thiocyanogen value<sup>7</sup> of the mixed fatty acids and the results have been found to be in agreement with those obtained by other methods (table 8).

### *Experimental*

The material under investigation was collected from the Central Provinces and obtained through Principal Surendra Mohan, Dayanand Ayurvedic College, Lahore. The fruits consist of 59.4 percent. of the pulp (mesocarp) and 40.6 percent. of the seed stones. The average weight of a seed stone is 2.3 grams and it consists of 78% of the stony shell and 22% of the kernels. The latter were white in colour having a characteristic smell and sweetish taste resembling that of almonds.

The moisture content of the kernels was 10.62% 50 grams of the kernels were completely incinerated in a porcelain dish when 2.1 grams (4.2%) of a greyish white ash were obtained containing the following radicles:—

Water soluble portion (20 %) —sodium, potassium, carbonate, chloride, and sulphate

Water insoluble portion (80%) —aluminium, calcium, magnesium, carbonate, sulphate and phosphate

50 Grams of the crushed kernels were successively extracted with various solvents in a soxhlet apparatus with the following results:—

1. *Petroleum ether* (40-60°C) —38.6%—The extract was light yellow in colour. On distilling off the solvent it gave a clear yellow thin oil.

2. *Ether* —2.17%—A light yellow coloured extract was obtained which on distilling off the solvent gave an oily residue mixed with some white solid mass.

3. *Chloroform* —0.47%—The extract gave a sticky resinous mass.

4. *Ethyl acetate* :—0.5%—The light brown extract gave a clear brown residue.

5. *Absolute alcohol* —2.8%—It gave a yellow extract from which a viscous oily residue was obtained. This gave tests for tannins and sugars.

For complete analysis, 5 kilograms of the crushed kernels were exhaustively extracted with petroleum ether (40-60°C), when 2 kilograms of a thin clear light yellow oil was obtained having a smell characteristic of the kernels.

The material left after removing the oil was dried to remove petroleum ether completely and then exhaustively extracted with 95% alcohol. The residue obtained on distilling off the alcohol is under examination, the results of which will be published in a separate communication.

#### *Examination of the Oil*

The oil obtained as above was purified with animal charcoal and Fuller's earth when a transparent light yellow non-drying oil was obtained, it deposited no residue on keeping. The characteristics of the oil are given in table 1:

TABLE I

	Hooper's results <sup>a</sup>	Shrikhande & Godbole <sup>b</sup>	Present authors
Specific gravity	at 15 °C 0.9168, 0.9193	0.9093	at 30 °C/30 °C 0.9108
Ref index		at 27 °C 1.4640	at 30 °C 1.4601 [ $\alpha$ ] <sub>30 °C</sub> + 0.04° 3.80
Rotation		Nil	
Acid value	2.48, 3.97		2.28
Saponification value	205.8, 205.4	181.0	198.80
Acetyl value		23.72	18.72
Iodine value	79.04, 85.38	97.0	89.14
Thiocyanogen value			65.0
Hehner value	94.2, 93.6	92.0	94.8
R M value	0.76, 0.78		0.82
Unsaponifiable matter		1.5	0.53%

The oil (500 grams) was saponified with alcoholic sodium hydroxide solution, unsaponifiable matter removed with ether and the soap solution was decomposed with dilute sulphuric acid when fatty acids having the following characteristics were obtained —

TABLE II

Consistency	<i>Solid</i>
Titre value	27 °C
Neutralisation value	202.99
Saponification equivalent	276.40
Iodine value	92.60
Thiocyanogen value	66.22

The mixed fatty acids were separated into 'solid' and 'liquid' acids by means of the differing solubility of their lead salts in alcohol (Twitchell's process)<sup>8</sup>, with the following results —

TABLE III

Acids	Percentage	Iodine value	Neutralisation value	Sap equivalent
Solid (saturated)	27.80	1.7	207.6	270.2
Liquid	72.20	128.4	199.4	281.3

#### Examination of Solid Acids

The methyl esters (79.1 gms) prepared from the 'solid' acids (80 grams) were fractionally distilled at 11 mm pressure from a Willstätter flask. The results of distillation, analysis and calculations<sup>9</sup> are given in table 4.

TABLE IV

No	Temp range°C	wt in gms	SV	SE	LV	Palmitic acid		Stearic acid		Unsaturated acids	
						%	gms	%	gms	%	gms
S1	upto 185	5 692	203 9	275 2	0 9	76 96	4 380	17 22	0 980	0 705	0 040
S2	185-190	24 404	200 9	279 4	1 2	63 24	15 440*	30 77	7 526*	0 892	0 218*
S3	190-195	8 735	199 5	281 5	1 4	55 89	4 885	38 03	5 321	1 090	0 095
S4	195-200	18 851	194 1	289 1	1 6	29 80	5 618*	64 18	12 100*	1 174	0 221*
S5	200-205	9 107	189 9	295 5	1 7	8 35	0 760	85 57	7 793	1 350	0 121
S6	205-210	7 297	187 8	298 7	2 1			93 67	6 834	1 640	0 120
S7	Residue - Loss	4 117 900	171 4	327 35	5 2				3 583		
		79 103					51 081		42 137		0 815

§ S7. Acids freed from unsaponifiable and decomposed matter, SE 285 0  
 \* S2 and S4, Components calculated from the results of refractionations (given below)

## Fraction S2

S2A	182-187	12 850	201 5	278 7	1 1	65 10	8 366	28 99	3 726	0 857	0 110
S2B	187-190	10 820	200 4	279 9	1 2	61 01	6 601	33 04	3 575	0 934	0 101
		23 670					14 967		7 301		0 211

## Fraction S4

S4A	193-196	8 950	194 5	288 5	1 4	31 79	2 845	62 24	5 571	1 090	0 098
S4B	196-200	8 600	193 6	289 7	1 6	27 72	2 384	66 19	5 693	1 250	0 108
		17 550					5 229		11 264		0 206

The esters from the different fractions were saponified and the liberated acids were fractionally crystallised from dilute acetone

*Fraction S<sub>1</sub>*—The acids, M P 53–54°C, on fractional crystallisation from acetone gave palmitic acid M P 61°C and stearic acid M P 66°C. The melting points were not depressed by the addition of authentic samples of these acids

*Fractions S<sub>2A</sub>, S<sub>2B</sub> and S<sub>3</sub>*—These fractions also gave palmitic acid M P 61°C and stearic acid M P 67°C and were confirmed as such by taking their mixed melting point with authentic samples

*Fractions S<sub>4A</sub>, S<sub>4B</sub>, and S<sub>5</sub>*—Palmitic and stearic acids were isolated and identified in these fractions

*Fractions S<sub>6</sub>*—The liberated acids M P 54°C gave only stearic acid on crystallisation, the melting point of which was not depressed by the addition of an authentic sample

*Fraction S<sub>7</sub>—Residue*—The acids were light yellow in colour. On extraction with petroleum ether (40–60°C) a product was obtained which after crystallisation was identified to be stearic acid (M P 66°C, S E 285)

The percentages of the individual solid acids in 'solid' acids and mixed acids are given in table V

TABLE V

Acids	% in solid acids	% in mixed acids
Palmitic	42.45	11.80
Stearic	57.55	16.00

### *Examination of the Liquid Acids*

The liquid acids on oxidation with an alkaline solution of potassium permanganate<sup>10</sup> gave a dihydroxy stearic acid (M P 130°C) and two tetrahydroxy stearic acids (M P 171° and 156°C) showing the presence of oleic and linoleic acids only

The quantitative determination of these acids was done by brominating<sup>11, 12</sup> a known weight in ether at –5°C, the results of which are recorded in table VI

TABLE VI

Weight of acids brominated	12.7160	gms
Weight of the tetrabromide (M.P. 114°C)	5.3002	"
Weight of the residue (di-+tetrabromides)	17.5759	"
Percentage of bromine in the residue (Piria and Schiff's method)	41.69	"
Weight of tetrabromide in the residue	5.6430	"
Weight of dibromide in the residue	11.9329	"
Total weight of the tetrabromide	10.9432	"
Weight of the linoleic acid	5.1060	"
Weight of oleic acid	7.6100	"
Percentage of oleic acid in liquid acids	59.85	"
Percentage of linoleic acid in liquid acids	40.15	"
Percentage of oleic acid in mixed acids	43.21	"
Percentage of linoleic acid in mixed acids	28.99	"

The 'liquid' acids (65 grams.) were converted into methyl esters (62.0 gms.) which were distilled under reduced pressure (9 mm). The results of distillation and calculation are given in table VII

TABLE VII

No.	Temp. range °C	wt in gms	Iod value	S E	Methyl oleate	Methyl linoleate
L1.	165-168	6.49	105.1	292.9	5.038	1.452
L2	168-170	9.97	131.1	294.4	4.750	5.220
L3	170-171	10.64	117.2	294.5	6.775	3.865
L4.	171-172	11.24	120.4	295.6	6.744	4.496
L5.	172-175	9.29	120.9	295.6	5.520	3.770
L6	175-180	9.36	120.0	296.3	5.659	3.701
L7	above-180	3.98	119.7	295.8	2.421	1.559
Loss		1.03				
		62.00			36.907	24.063

Percentage of oleic acid in 'liquid' acids	60.53
Percentage of linoleic acid in 'liquid' acids	39.47
Percentage of oleic acid in mixed acids	43.70
Percentage of linoleic acid in mixed acids	28.50

The acids from the various fractions are oxidised by alkaline potassium permanganate solution<sup>11</sup>: Dihydroxy stearic acid (M.P. 130°C) and tetrahydroxy stearic acids (M.P. 156° and 171°C) were isolated from the



oxidation products showing thereby the presence of oleic and linoleic acids in the various fractions

The percentages of oleic and linoleic acids in mixed acids calculated from their thiocyanogen and iodine values are given below for comparison with the results obtained by bromination and ester fractionation methods

TABLE VIII

Acids	Percentage by bromination method ( <i>loc cit</i> )	% by ester fractionation method	% calculated from SCN value and I V of mixed acids
Linoleic	28.99	28.50	29.12
Oleic	43.21	43.70	44.30

#### EXAMINATION OF THE SOAP

The iodine value of the oil (89.14) and the titre value of the mixed acids of the oil (27°C) are very similar to those of ground nut oil (titre value 28°C and I V 90.108), which is very widely used in the manufacture of washing soaps. The washing soap prepared from a mixture of 40% *Terminalia belerica* oil and 60% ground nut oil was found to give good results by practical tests\*. The ground nut oil on hydrogenation is largely used in the preparation of toilet soaps. The *Terminalia belerica* oil could, therefore, be similarly used after hydrogenation as its properties are so similar to those of ground nut oil. The possibility of the industrial utilisation is thus indicated, and we reserve it for future study.

#### EXAMINATION OF THE UNSAPONIFIABLE MATTER

The unsaponifiable matter obtained by extracting the soaps with ether and distilling off the solvent was resaponified in order to free it from any adhering oil. On crystallisation from rectified spirit it gave a white solid melting at 135–136°C. The acetyl derivative melted at 124°C. It was identified to be phytosterol by colour reactions. Thus the sterol is sitosterol commonly found in most vegetable oils.

\* These practical tests were carried out by the soap expert, Mr P. S. Menon, Senior Chemical Assistant in charge of the Industrial Chemistry Section, Department of Industries, Bihar, Patna, to whom our thanks are due.

*Acknowledgement*

We wish to make a grateful acknowledgement to the Kanta Prasad Research Scholarship Endowment Trust of the United Provinces for the award of a research scholarship to one of us (B S) which has enabled him to take part in this investigation and also to the University of Allahabad for providing research facilities

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# THE TIME OF SETTING AND CHANGES IN H-ION CONCENTRATION DURING THE SETTING OF NICKEL HYDROXIDE GELS FORMED BY THE ADDITION OF ELECTROLYTES TO THE NICKEL HYDROXIDE SOL

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The time of setting ( $T$ ) of the nickel hydroxide gels in the presence of varying quantities ( $A$ ) of different electrolytes has been measured at  $35^\circ$  and it has been found to follow the relation  $T = RA^{-m}$ , in which  $m$  and  $R$  are constants. The order of different electrolytes is



The  $pH$  of gel forming mixtures has been found to increase during gelation. The increase is largest in the early period of gelation and it decreases in the later stages.

It is now well known that one of the principal methods of preparation of inorganic gels is by the addition of electrolytes to a fairly concentrated sol, dialysed or undialysed, of the gel-forming substance. Thus transparent gels of ferric,<sup>1</sup> chromium and stannic,<sup>2</sup> ceric<sup>3</sup> and zirconium<sup>4</sup> hydroxides, of vanadium pentoxide,<sup>5</sup> and of ferric and chromium arsenate,<sup>6</sup> have been obtained.

It has been observed that in certain cases it is not quite necessary to use concentrated sols, for example, Grimaux<sup>1</sup> obtained ferric hydroxide and Ravinervon<sup>7</sup> the vanadium pentoxide gels by using fairly dilute sols of these substances.

It is, however, quite necessary to use solutions of electrolytes of concentrations lying within certain definite range, and if these limits are exceeded either no gel is formed, or a gelatinous precipitate is obtained. These conclusions have been experimentally confirmed by Weiser<sup>2</sup> in the case of stannic hydroxide gels.

The time of setting of gels prepared by this method has been measured by Prakash and coworkers<sup>8</sup> who have also examined the effects of the concentration of the sol and of the electrolytes added, on the time of setting. They found that the time of setting ( $\theta$ ) is related to the concentration of electrolyte ( $c$ ) as  $\theta = RC^{-p}$  in which  $R$  and  $p$  are constants. Previously Prasad and Hattiangadi had shown that the time of setting ( $T$ ) of silicic acid gels is related to the concentration ( $C$ ) of ammonium acetate solution as

$$(T - ac^m)(T - bc^{-n}) = 0$$

The expression in the second bracket is of the same form as obtained by Prakash and co-workers<sup>8</sup>

In this investigation the time of setting of gels of nickel hydroxide formed by the addition of electrolytes to the nickel hydroxide sol prepared by a new method, has been measured and the effect of the concentration of electrolyte added on the setting time has been examined. The changes in the H-ion concentration during the formation of some of these gels have also been measured.

These gels were first prepared by Tower and Cook<sup>10</sup> by the addition of normal alcoholic solution of  $KOH$  to a glycerol solution of nickel acetate. Later they found that transparent gels are obtained if  $NaOH$  or  $KOH$  is added to a concentrated solution of nickel tartrate. The author has found that the gel obtained by the addition of  $NaOH$  solution to a saturated solution of nickel hydroxide in tartaric acid gives rise to a stable, transparent green coloured sol when it is immediately shaken with suitable amount of distilled water. This sol sets to a transparent gel when suitable amounts of certain electrolytes are added to it.

## EXPERIMENTAL

### *Preparation of the nickel hydroxide sol*

Approximately 2.0 N- $NaOH$  solution was added to the nickel chloride solution (30g. in 300cc of water) until the mixture was distinctly alkaline. The precipitated nickel hydroxide was washed with distilled water, until free from chloride ions and then dissolved in 30g of tartaric acid. The required amount of 2.0N- $NaOH$  was then added to the clear solution which rapidly set to a clear transparent gel, which, on shaking with distilled water, dispersed completely and gave rise to a stable transparent green

coloured sol. The colloidal content of the sol corresponded to 0.30/g. of nickel in 100 cc of the sol

### *Solution of electrolytes*

The electrolytes used were solutions of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{HgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{AlCl}_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{HCl}$ , prepared from pure chemicals in distilled water.

### *Method of measuring the time of setting*

The time of setting was measured at  $35^\circ$  in an air thermostat by Hurd and Letteron's method<sup>11</sup>, in which certain modifications were introduced for the sake of accuracy

### *Experimental procedure*

A number of test tubes were filled with 5 cc of the nickel hydroxide sol and another set with different known volumes of the solutions of an electrolyte diluted with distilled water so as to make up their volume to 5 cc. Both sets were put in the air thermostat for half an hour to attain the constant temperature. The sol and electrolyte solution were then mixed a number of times and well shaken. The mixture was then transferred to a small weighing bottle, and a glass rod 3" long and 1 mm in diameter was inserted in position, a stop watch was also started simultaneously. A number of readings of the time of setting were taken, each time disturbing the gel-forming mixture as few times as possible. The minimum time obtained in this manner was taken as the time of setting of the gel.

The small volumes of the solution of electrolytes used in this investigation were measured out from a micropipette measuring up to 0.01 cc.

### *Measurement of pH*

The pH values of the gel-forming mixtures were determined by Coleman's electrometer, which was standardised and occasionally checked with the freshly prepared standard buffer solutions

### *Results*

The results obtained are given in the following tables in which  $A$  = cc of electrolyte solutions added to the sol,  $T$  = time of setting in minutes.

The range of the change in the pH during and after the setting period are given in the third column of the Tables.

TABLE I  
Electrolyte NaCl (1 oN)

A	T	pH	log A	log T (Obs)	log T (Cal)
2 200	4 0	8 37-8 39	0 3424	0 6021	0 731
2 100	5 5		0 3222	0 7404	0 708
2 050	8 0		0 3118	0 9031	0 904
2 000	12 0		0 3010	1 0792	1 106
1 975	16 5	8 30-8 35	0 2956	1 2175	1 210
1 950	20 5		0 2900	1 3118	1 312
1 925	25 5		0 2844	1 4065	1 418
1 900	34 0		0 2788	1 5378	1 522
1 850	60 0		0 2672	1 7782	1 753

$m_1=18.75$        $\log R_1=6.75$

TABLE II  
Electrolyte  $Na_2SO_4$  (0.2N)

A	T	pH	log A	log T (Obs)	log T (Cal.)
5 00	2 0		0 6990	0 3010	0 3630*
4 85	3 0		0 6857	0 4771	0 5000*
4 75	4 0		0 6767	0 6021	0 6020*
4 65	5 0		0 6675	0 6990	0 7020*
4 55	6 0	8 31-8 36	0 6580	0 7782	0 7970*
4 45	8 0		0 6484	0 9031	0 9070*
4 35	10 0		0 6385	1 0000	1.0500
4 25	20 0		0.6284	1 3010	1 3100
4 15	37 0	8 15-8 21	0 6180	1 5682	1 5700
4 00	65 0	.	0 6021	1 8129	1 9900

$m_1=25.69$

$\log R_1=17.45$

$*m_2=10.69$

$*\log R_2=7.83$

TABLE III

Electrolyte  $HgCl_2$  (0.1 N)

A	T	pH	log A	log T (Obs)	log T (Cal)
2.00	0.75	7.31-7.59	0.3010	-0.1249	-0.2500
1.80	1.00		0.2533	0.0000	-0.0300
1.60	2.0		0.2041	0.3010	0.2610
1.40	3.5		0.1461	0.5441	0.5901
1.30	6.0		0.1139	0.7782	0.7731
1.20	10.0		0.0792	1.0000	0.9702
1.10	15.5		0.0414	1.1903	1.1848
1.00	23.0		0.0000	1.3617	1.4200
0.90	65.0		-0.0456	1.8129	1.6801

 $m_1=5.68$  $\log R_1=1.42$ 

TABLE IV

Electrolyte  $BaCl_2$  (0.025 N)

A	T	pH	log A	log T (Obs)	log T (Cal)
2.50	0.25	8.37-8.44	0.3979	-0.6021	-0.6000
2.45	0.50		0.3892	-0.3010	-0.3000
2.40	1.00		0.3802	0.0000	0.010
2.35	2.0		0.3711	0.3010	0.330
2.30	3.0		0.3617	0.4771	0.660
2.25	7.0		0.3522	0.8451	0.990
2.20	12.0		0.3424	1.0792	1.330
2.150	20.0		0.3324	1.3010	1.670
2.125	30.0		0.3273	1.4771	1.850
2.100	90.0		0.3222	1.9542	2.000

 $m_1=34.61$  $\log R_1=13.17$

TABLE V  
Electrolyte  $\text{CaSO}_4$  (N/30)

A	T	pH	log A	log T (Obs.)	log T (Cal.)
2 50	1 0		0 3979	0 0000	0 1300*
2 40	2 0		0 3802	0 3010	0 298*
2 30	3 0		0 3617	0 4771	0 474*
2 20	4 5		0 3424	0 6532	0 657*
2 10	7 0		0 3222	0 8451	0 849*
2 00	12 0	8 70-8 82	0 3010	1 0792	1 050*
1 90	18 0	8 68-8 82	0 2788	1 2553	1 261
1 80	23 0	8 67-8 82	0 2553	1 3617	1 362
1 70	30 0	8 63-8 82	0 2304	1 4771	1 477

$$m_1=4.63$$

$$*m_2=9.50$$

$$\log R_1=2.55$$

$$*\log R_2=3.91$$

TABLE VI  
Electrolyte:  $\text{AlCl}_3$  (0.05N)

A	T	pH	log A	log T (Obs.)	log T (Cal.)
3 60	0 50		0 5563	-0 3010	-0 3000*
3 50	0 75		0 5441	-0 1249	-0 0700*
3 40	1 50		0 5315	0 1761	0 18*
3 30	3 0		0 5185	0 4771	0 44*
3 20	3 5		0 5051	0 7404	0 68*
3 10	7 5		0 4914	0 8751	0 70
3 00	10 5	7 18-7 51	0 4771	1 0212	0 92
2 90	15 0	7 35-7 71	0 4624	1 1761	1 14
2 80	22 5	7 35-7 76	0 4472	1 3522	1 36
2 70	40 0	7 51-7 84	0 4314	1 6021	1 59
2 60	70 0		0 4150	1 8451	1 84
2 50	hrs	.	..	..	

$$m_1=14.82$$

$$*m_2=19.23$$

$$\log R_1=7.99$$

$$*\log R_2=10.40$$



TABLE VII

Electrolyte :  $Al_2(SO_4)_3$  (0.05N)

A	T	pH	log A	log T (Obs)	log T (Cal)
3 60	0 5		0 5563	-0 3010	-0 23*
3 50	1 0		0 5441	0 0000	-0 06*
3 40	1 75		0 5315	0 2430	0 22*
3 30	3 0		0 5185	0 4771	0 50*
3 20	5 5		0 5051	0 7401	0 80*
3 10	7 5		0 4914	0 8751	0 75
3 00	10 5	7 18-7 60	0 4771	1 0212	1 06
2 90	16 0	7 18-7 68	0 4624	1 2041	1 17
2 80	23 0	7 31-7 83	0 4472	1 3617	1 38
2 70	42 0	7 38-7 89	0 4314	1 6232	1 61
2 60	72 0	...	0 4150	1 8573	1.84

$$m_1=14.28$$

$$\log R_1=7.77$$

$$*m_2=21.94$$

$$*\log R_2=11.90$$

TABLE VIII

Electrolyte  $HCl$  (0.1N)

A	T	pH	log A	log T (Obs.)	log T (Cal)
2 58	1 0		0 4116	0 000	-0 16*
2 56	1 3		0 4082	0 114	0 10*
2 54	2 5		0 4048	0 398	0 38*
2 52	4 5		0 4014	0 653	0 65*
2 50	7 0		0 3979	0 845	0 82
2 48	10 0	7 50-7 83	0 3945	1 000	1 01
2 46	14 0	7 46-7 83	0 3909	1 146	1 20
2 45	20 0	7 52-7 84	0 3892	1 301	1.30
2 44	40 0		0 3874	1 602	1 38

$$m_1=53.09$$

$$\log R_1=21.95$$

$$*m_2=79.30$$

$$*\log R_2=32.48$$

## Discussion of Results

The gels obtained by the addition of all the electrolytes used were firm and transparent, excepting in the case of  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  which are required in high concentration.

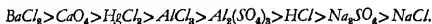
The foregoing tables show that the time of setting decreases at first rapidly and then slowly as increasing amounts of electrolytes are added to the same amount of the nickel hydroxide sol

The concentrations ( $x$ ) of various electrolytes in the gel-forming mixtures required to cause the setting in 20 minutes have been read from the curves drawn by plotting ( $A$ ) against ( $T$ ) and are given in Table IX

TABLE IX

Electrolytes	$X$	Electrolytes	$X$
$\text{NaCl}$	0.195N	$\text{AlCl}_3$	0.014N
$\text{Na}_2\text{SO}_4$	0.085N	$\text{HgCl}_2$	0.010N
$\text{HCl}$	0.024N	$\text{CaSO}_4$	0.006N
$\text{Al}_2(\text{SO}_4)_3$	0.014N	$\text{BaCl}_2$	0.005N

The order of these electrolytes is thus



This series does not follow the valency rule according to which the gelating power (analogous to coagulating power) of trivalent aluminium salts should be the highest. Such exceptions have been found in the study of the coagulating power of electrolytes in the case of several sols.

On plotting  $\log A$  against  $\log T$  a single straight line or two intersecting straight lines, are obtained. The results, therefore, in general, show that  $T = R A^{-m}$  where  $m$  and  $R$  are constants. The values of  $m$  and  $\log R$  are given below each of the tables I-VIII and summarised in Table X in which  $m_1$  and  $\log R_1$  refer to straight lines corresponding to lower concentrations of an electrolyte and  $m_2$  and  $\log R_2$  for those corresponding to

higher concentrations. The latter values are marked with an asterisk in each case.

TABLE X

Electrolyte	$m_1$	$\log R_1$	$m_2$	$\log R_2$
<i>NaCl</i>	18.75	6.75		
<i>Na<sub>2</sub>SO<sub>4</sub></i>	25.69	17.45	10.69	7.83
<i>HgCl<sub>2</sub></i>	5.68	1.42*		
<i>BaCl<sub>2</sub></i>	34.61	13.17		
<i>CaSO<sub>4</sub></i>	4.63	2.55	9.50	3.91
<i>AlCl<sub>3</sub></i>	14.82	7.99	19.23	10.40
<i>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub></i>	14.28	7.77	21.94	11.90
<i>HCl</i>	53.09	21.95	79.30	32.48

It will be seen that excepting for aluminium salts the values of  $m$  and  $\log R$  are different for different electrolytes.

These values of  $m$  and  $\log R$  have been used to calculate the values of  $T$  for the corresponding values of  $A$  employed in this investigation and the results obtained are given in the 6th column of the Tables I-VIII. The values marked with an asterisk are calculated from  $m_2$  and  $\log R_2$ . A comparison of the calculated and observed values of  $T$  shows that the relation  $T = RA^{-m}$  reproduces the experimental results fairly accurately.

The changes in  $pH$  during and after the setting of the gels were observed with all electrolytes excepting *NaCl* and *Na<sub>2</sub>SO<sub>4</sub>*. The  $pH$  increases for some time and then reaches a constant value. These results are similar to those obtained by Kugelmass.<sup>12</sup>

Also the  $pH$  ceases to change earlier, greater is the concentration of the electrolyte added. This is illustrated in the case of gels formed by the addition of aluminium sulphate, in Table XI, in which ' $t$ ' represents the interval in minutes after introducing the mixture in the electrometer, at which the  $pH$  readings were taken.

TABLE XI

$t$	$A=2.70$ $pH$	$A=2.80$ $pH$	$A=2.90$ $pH$	$A=3.00$ $pH$
1 0	7.38	7.31	7.28	7.18
2 5	7.54	7.48	7.47	7.38
5 0	7.67	7.60	7.56	7.47
7 5	7.71	7.66	7.60	7.51
10 0	7.74	7.69	7.63	7.54
12 5		7.71	7.65	7.57
15 0	7.79	7.73		7.60
17 5			7.68	No change
20 0	7.81	7.76	No change	
25 0	7.83	7.78		
35 0	7.85	7.80		
45 0	7.87	7.82		
60 0	7.89	7.83		
70 0	No change	No change		
T	42 0	23 0	16 0	10 5

Tables I to VIII reveal that mixtures containing greater amounts of electrolytes set earlier. It may, therefore, be surmised that the changes in  $pH$  are related in some way to the process of setting of these gels. It will be seen from the table XI that the rapid increase in  $pH$  takes place during the early period of gelation process, that is, in the first few minutes. This is probably the stage of coagulation of the sol. The slow increase in  $pH$  which takes place in the later period of gelation process and continues even after the gel has set, probably occurs during the formation of specific gel-structure.

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## CHEMICAL EXAMINATION OF *SPHAERANTHUS INDICUS*, LINN PART I—THE COMPONENT FATTY ACIDS AND PRO- BABLE GLYCERIDES OF THE FATTY OIL

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*Sphaeranthus indicus* Linn has been found to yield 5.03% of a semi-drying oil having  $d_{40}^{20}$  0.9298,  $n_D^{25}$  1.4882, acid value 13.97, sap value 179.40, acetyl value 25.75, Hehner value 90.33, unsaponifiable matter 1.81%, R. M. 1.24, iodine value (Hanus) 117.40 and thiocyanogen value (24 hours) 80.50

The component fatty acids were found to be linolenic 1.02%, linoleic 46.08%, oleic 44.32%, palmitic 1.06%, stearic 5.70% and arachidic 1.82%. The unsaponifiable matter consisted of a sitosterol m.p. 135°C and another compound, m.p. 78°C

The glyceride structure of the fatty oil has been determined by brominating the neutral oil, separating the bromoglycerides into simpler fractions and estimating their fatty acid composition. The component glycerides of the oil are—palmitodilinolein (0.8%), stearodilinolein (4.1%), arachidodilinolein (1.3%), palmitooleolinolein (1.5%), stearooleolinolein (7.9%), arachidooleolinolein (2.5%), palmitodilolein (1.1%), stearodilolein (6.0%), arachidodilolein (1.9%), linoleooleolinolein (3.0%), trilinolein (3.1%), oleodilinolein (32.9%), dioleolinolein (33.6%) and triolein (0.3%)

*Sphaeranthus indicus* Linn commonly known as Mundi or Gorakh-mundi in Hindi and Mahamundi in Sanskrit is a much branched annual herb belonging to the natural order compositae. The herb is very common in the rice fields of India where it grows in abundance after the rice is harvested. It is also distributed throughout India, Ceylon, China, and Africa

The drug generally consists of the whole plant or only capitulas and has been described by various writers to be highly medicinal. According to Kirtikar and Basu,<sup>1</sup> Chopra<sup>2</sup> and Dymock, Warden and Hooper<sup>3</sup> the herb is bitter, laxative, tonic, anthelmintic and appetiser, useful in insanity, indigestion, anaemia, dysentery, scabies and ringworm and enriches blood. The aqueous distillate of the herb is the most common preparation used.

In spite of the great medicinal value of the plant, very little work has

been done on its chemical examination Dymock (*loc. cit*) reports that on distillation with water the herb yields a dark sherry coloured essential oil and that the most important principle that could be detected in the leaves, stems and flowers was a bitter alkaloid provisionally named 'Sphaeranthine' The constants of the essential oil have also been recently reported<sup>4</sup> and will be compared with those obtained by us in a subsequent communication It was, therefore, thought desirable that a complete systematic chemical examination of the drug would be interesting and with this object in view the present work was undertaken In this part the work on the component acids and glyceride structure of the fatty oil is described The results of the examination of the other constituents of the drug will form the subject of subsequent communications

The material was so light and voluminous that the use of petroleum ether or benzene for the extraction of the fatty oil was found to be too expensive The difficulty was further aggravated by the low percentage yield of the oil The whole material was, therefore, extracted with rectified spirit in lots of 600 grams The alcohol was distilled off and from the residue fatty oil was separated by the method described in the experimental part

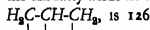
A detailed chemical examination of the oil has shown that it consists of the glycerides of linolenic (1.02%), linoleic (46.08%), oleic (44.32%), palmitic (1.06%), stearic (5.7%) and arachidic (1.82%) acids, together with an unsaponifiable matter consisting of a sitosterol m.p. 135° and another compound m.p. 78°C

The component glycerides of the oil have been examined by brominating the neutral oil in petroleum ether (B.P. 40°-60°C) at 5°C and resolving the brominated product into a number of simpler fractions<sup>5,6,7</sup> The absence of any fully saturated or disaturated glyceride was established by chilling the oil in acetone solution in a refrigerator for about a week when only 0.2 gms. of the unsaponifiable matter was deposited A similar small quantity of the unsaponifiable matter was obtained on oxidising the neutral oil in acetone with powdered potassium permanganate according to the method of Hilditch and Lea,<sup>8</sup> confirming further the absence of any fully saturated glyceride.

The component acids of the oil<sup>\*</sup> determined by this method are in fair agreement with those obtained by lead salt separation and ester fractionation methods. The comparison is shown in table 12.

The probable component glycerides of the oil are as follows :—

palmitodilinolein (0.8%), stearodilinolein (4.1%), arachidodilinolein (1.3%) palmitooleolinolein (1.5%), stearoleolinolein (7.9%), arachidooleolinolein (2.5%), palmitodiolein (1.1%), stearodiolein (6.0%), arachidodiolein (1.9%), linoleoololinoleincin (3%), trilinolein (3.1%), oleodilinolein (32.9%) dioleolinolein (33.6%) and triolein (0.3%) Our experiments have thus shown the actual number of glycerides to be 14, whereas the maximum number of individual glycerides, which may be obtained by any permutation of the six fatty acids in combination with the trihydric glyceryl radical,



### EXPERIMENTAL

About twenty kilograms of the crushed material was extracted with rectified spirit. The syrupy mass left after distilling off the alcohol was subjected to steam distillation whereby the volatile oil was removed. Now there remained in the distilling flask an aqueous layer and above it an oily layer. The oily layer was separated from the aqueous layer with a separating funnel. This was then treated with petroleum ether (B.P. 40-60°C) which dissolved out the fatty oil. On distilling off the solvent a dark viscous oil was obtained which was further purified with animal charcoal and Fuller's earth. The oil did not deposit any residue on keeping. It was found to be a semidrying oil having the following physical and chemical constants (Table I) :—

TABLE I

Yield	5.03%
Specific gravity $\frac{\text{oil } 30^\circ\text{C}}{\text{water } 30^\circ\text{C}}$	0.9298
Refractive index at 25°C	1.4882
Acid value	13.97
Saponification value	179.40
Acetyl value	21.75
Hehner number	90.33
Reichert Meissl value	1.24
Unsaponifiable matter	1.85%
Iodine value (Hanus)	117.40
Thiocyanogen value (24 hours)	80.50

Four hundred and seventy-five grams of the oil were then saponified with an alcoholic solution of sodium hydroxide, alcohol distilled off and the

unsaponifiable matter removed with ether. The soap solution was then decomposed with dilute sulphuric acid when fatty acids (425 grams) having the following constants were obtained (Table 2).—

TABLE 2

Consistency	—liquid, became solid on keeping.
Neutralisation value	—194 20
Saponification equivalent	—288 95
Iodine value (Hanus)	—123 32
Thiocyanogen value (24 hours)	- 83 85

The mixture of fatty acids was then separated into solid and liquid acids by the Twitchell's Lead Salt-Alcohol process<sup>9</sup>. The percentages, the iodine and thiocyanogen values, the neutralisation values and the saponification equivalents of the solid and liquid acids are given below (Table 3):—

TABLE 3

Acids	%	Iodine value	Thiocyanogen value	Neutralisation value	Saponification equiv.
Solid	8 58	0 88	—	189 90	295 40
Liquid	91 42	136 00	90 86	200.30	180 20

#### EXAMINATION OF THE LIQUID ACIDS

Ten grams of the liquid acids were oxidised with a dilute solution of alkaline potassium permanganate according to the method of Lapworth and Mottram<sup>10</sup> when a dihydroxy stearic acid M.P. 130°C, a tetrahydroxy-stearic acid M.P. 172°C and a hexahydroxy stearic acid M.P. 202°C were obtained showing the presence of oleic, linoleic and linolenic acids in the liquid acids.

The quantitative determination of these acids was done by brominating a known weight of these acids in ether at 10°C according to the method of Eibner and Muggenthalor<sup>11</sup> modified by Jamieson and Boughmann,<sup>12</sup> the results of which are given below (Table 4):—

TABLE 4

Weight of liquid acids	8.6896 gms.
Weight of linolenic hexabromide	0.1622 gms.
Melting point of linolenic hexabromide	176°C



Weight of linoleic tetrabromide	5 8965 gms
Melting point of linoleic tetrabromide	113 °C
Weight of the residue (di-+tetrabromide)	9 9416 gms
Bromine contents of the residue (Piria and Schiff's method)	42 05%
Weight of linoleic tetrabromide in the residue	3 4030 gms
Weight of oleic dibromide in the residue	6 5386 gms
Total weight of linoleic tetrabromide	9 2995 gms
Weight of linolenic acid	0 0962 gms
Weight of linoleic acid	4 3400 gms
Weight of oleic acid	4 1730 gms

From the above results the percentages of linolenic, linoleic and oleic acids in liquid acids, in mixed acids and in the oil have been calculated and are given below (Table 5) —

TABLE 5

Acids	Percentage in liquid acids	Percentage in mixed acids	Percentage in oil
Linolenic . . .	1 12(0 72)	1 02	0 92
Linoleic . . .	50 41(49 03)	46 08	41 62
Oleic . . .	48.47(50 25)	44 32	40 03

The figures in brackets are those calculated for these acids from the thiocyanogen value of the liquid acids

The theoretical iodine value of a mixture of 1 12% linolenic, 50.41% linoleic and 48 47% oleic acids is 137 92 which agrees fairly well with the iodine value of liquid acids (Table 3)

The percentages of linolenic, linoleic and oleic acids in the mixed acids were calculated from the thiocyanogen and iodine values of mixed acids. These results are given below (Table 6) for comparison with those obtained by bromination of the liquid acids

TABLE 6

Acids	Percentage in mixed acids by bromination method	Percentage in mixed acids by calculation from thiocyanogen and iodine values
Linolenic	1 02	1 11
Linoleic	46.08	43 61
Oleic	44 32	46 69

## EXAMINATION OF THE SOLID ACIDS

The solid acids were rubbed over a porous plate to free them from traces of liquid acids. They were found to melt at  $58^{\circ}\text{C}$ . The acids (38 grams) were then converted to methyl esters in the usual manner when 40 grams of the mixed esters were obtained. The esters were subjected to distillation under reduced pressure, the results of which are given below (table 7) —

TABLE 7

Fraction No	Weight of esters distilled—39.88 gms		
	Pressure	Boiling range	Weight in grams
1	13 mm	187-190°C	2.70
2	13 mm	190-193°C	12.42
3	13 mm	193-197°C	10.37
4	13 mm	197-200°C	6.95
5	13 mm	200-205°C	2.64
6 (Residue)			4.28

The saponification value, the saponification equivalent and the iodine values of all the fractions were determined and the amounts of various acids in different fractions were calculated according to the method of Jamieson and Boughmann<sup>13</sup> (Table 8).—

TABLE 8

Fraction number	Iodine value	Saponification value	Saponification equivalent	Palmitic acid		Stearic acid		Arachidic acid		Unsaturated acids	
				%	gms	%	gms	%	gms	%	gms
1	0.31	203.9	275.2	77.02	2.080	17.65	0.477			0.23	0.006
2	0.52	191.9	292.4	13.54	2.302	76.28	9.473			0.38	0.047
3	0.84	185.7	302.3			80.83	3.381	13.92	1.443	0.62	0.064
4	0.79	181.0	309.8			54.13	3.761	40.77	2.833	0.58	0.040
5	0.95	180.9	310.1			53.73	1.419	41.05	1.083	0.70	0.018
Unpolymerised (2.257 gms)											
6 Residue Polymerised (2.003 gms)	1.04	172.1	336.1					94.95	2.143	0.76	0.017
TOTAL					4.382		23.511		7.502		0.192

*Fraction 1* The liberated acids from this fraction melted at  $59^{\circ}\text{C}$ . On repeated crystallisation from acetone palmitic acid, M.P.  $60-61^{\circ}\text{C}$  and stearic acid M.P.  $65-66^{\circ}\text{C}$  were isolated. These melting points were not depressed by the addition of pure palmitic and stearic acids respectively.

*Fraction 2* The acids obtained after saponification of the fraction melted at  $60^{\circ}\text{C}$ . Fractional crystallisation from acetone gave palmitic acid M.P.  $61^{\circ}\text{C}$  and stearic acid M.P.  $65-66^{\circ}\text{C}$ , not depressed by the addition of authentic samples of these acids.

*Fractions 3, 4 and 5* The liberated acids from these fractions had melting points  $64^{\circ}\text{C}$ ,  $64^{\circ}\text{C}$  and  $70^{\circ}\text{C}$  respectively. They were fractionally crystallised from acetone when in each case stearic acid, M.P.  $66^{\circ}\text{C}$  and arachidic acid, M.P.  $74^{\circ}$  were obtained. The presence of stearic acid was confirmed by the determination of mixed melting point with an authentic sample, but that of arachidic acid could not be confirmed for want of an authentic sample.

*Fraction 6 (Residue)* The acids liberated from this fraction after saponification were brown in colour. On extracting this with petroleum ether an acid was obtained which had molecular weight 310.6. The acid on crystallisation from acetone melted at  $74-75^{\circ}\text{C}$  and was evidently pure arachidic acid.

*Confirmation of arachidic acid* The mixed melting points of the arachidic acid from fractions,  $F_3$ ,  $F_4$ ,  $F_5$  and  $F_6$  with one another were determined and found to be undepressed. The different samples of arachidic acid from all the fractions were then mixed and crystallised from acetone, and melted at  $75^{\circ}\text{C}$ . This was converted into silver salt and ignited. 0.6810 gms of silver salt gave 0.1739 gms of silver. (Found molecular weight 314.9,  $\text{C}_{20}\text{H}_{40}\text{O}_2$  requires M.W. 312).

The percentages of various solid acids in mixed solid acids, in mixed acids and in the oil are given below (Table 9):—

TABLE 9

Acid	Percentage in solid acids	Percentage in mixed acids	Percentage in oil
Palmitic	12.38	1.06	0.96
Stearic	66.43	5.70	5.15
Arachidic	21.19	1.82	1.64

## EXAMINATION OF THE UNSAPONIFIABLE MATTER

The unsaponifiable matter obtained by extracting the soap solution with ether was a semi-solid yellow brown mass having a characteristic odour. This was kneaded in petroleum ether (B.P. 40-60°C) and kept in a frigidaire. The portion insoluble in petroleum ether was crystallised from absolute alcohol whereby a white crystalline substance M.P. 78° was obtained. This gave no test for sterol and will be described fully in a later communication.

The petroleum ether soluble portion on repeated crystallisation from alcohol gave a solid crystalline compound M.P. 135°C. This gave all colour tests for a phytosterol, sitosterol. The acetyl derivative melted at 122°C. Hence this compound is a phytosterol, sitosterol, found in most vegetable oils.

## THE COMPONENT GLYCERIDES

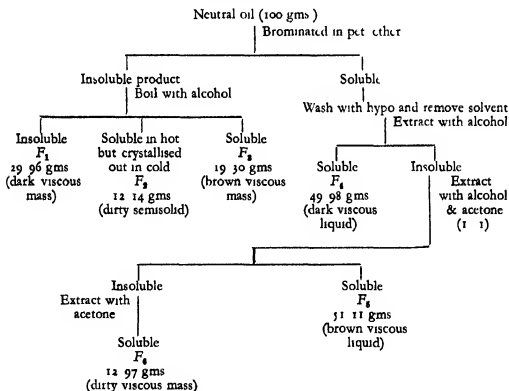
The oil was made neutral by treating it with sodium carbonate and purified with animal charcoal and Fuller's earth.

Fifty grams of the neutral oil were then dissolved in six times its weight of dry acetone and chilled at 0°C in a frigidaire for about six days, when 0.2 gm. of a neutral substance was deposited. This was filtered off and crystallised from alcohol when a white crystalline substance M.P. 74°C was obtained. This was found to be the unsaponifiable matter. Hence the oil does not contain any appreciable quantity of fully saturated or disaturated glycerides.

Fifty grams of the neutral oil were then dissolved in ten times its weight of dry acetone and oxidised with four times its weight of powdered potassium permanganate according to the method of Hilditch and Lea (*loc. cit.*). The process was repeated three times when in the end 0.2 gm. of a neutral substance was obtained which on crystallisation from alcohol melted at 75°C. This was found to be impure unsaponifiable matter. This further confirms the absence of any fully saturated glycerides.

One hundred grams of the neutral oil were then dissolved in a litre of dry petroleum ether (B.P. 40-60°C), cooled to -5°C and bromine added till it was in slight excess which was indicated by the colour of the solution turning to permanently brown. This was kept overnight in a frigidaire when some gummy solid mass separated. This was filtered off and washed

with chilled petroleum ether. The solid mass left on the filter paper was boiled with alcohol when a portion remained undissolved which was designated as  $F_1$ , another part crystallised out on cooling and this was  $F_2$  and a third part  $F_3$  was obtained on distilling off alcohol. The petroleum ether filtrate was treated with a solution of sodium thiosulphate to remove excess of bromine, washed with water, dehydrated over fused calcium chloride and the solvent distilled off, when a dark viscous liquid was obtained. This was extracted with absolute alcohol and the alcohol soluble portion was designated as  $F_4$ . The alcohol insoluble portion was treated with a mixture of alcohol and acetone (1 : 1) and the soluble portion gave  $F_5$ . The remaining insoluble portion then completely dissolved in acetone giving  $F_6$ . The scheme of separation is shown below —



The fractions  $F_1$ ,  $F_2$ ,  $F_3$ ,  $F_4$ ,  $F_5$  and  $F_6$  were all debrominated by taking them in methyl alcohol, adding zinc dust, saturating the solution with dry hydrochloric acid gas and then refluxing for about eight hours. The debrominated products were then saponified with alcoholic potassium

hydroxide, the unsaponifiable matter removed with ether and the fatty acids liberated with dilute sulphuric acid. The saponification equivalent, the iodine value and the thiocyanogen value of the liberated acids were then determined and from these values the quantities of individual acids were calculated. The amounts of saturated acids being too small for estimating them separately, they were considered as one acid. The fractions were then oxidised with a dilute alkaline solution of potassium permanganate according to the method of Lapworth and Mottram (*loc cit*) the unoxidisable product extracted with petroleum ether and the saponification equivalent of the acids so obtained were determined. It was found that no saturated acid was present in  $F_1$ , but from the oxidation product a hexahydroxystearic acid was isolated besides tetra- and di-hydroxy stearic acids, showing thereby that the acids of  $F_1$  contain linolenic, linoleic and oleic acids only. As the hexahydroxy stearic acid could not be isolated from the oxidation product of any other fraction, it is clear that the entire linolenic acid is present in  $F_1$ . The amounts of these three acids in  $F_1$ , were then calculated by the usual formula.

The results of bromination and analysis are given below in tables 10, 11 and 12

TABLE 10

	$F_1$	$F_2$	$F_3$	$F_4$	$F_5$	$F_6$
Weight of brominated product in gms	29.96	12.14	19.30	49.98	51.11	12.97
Weight of debrominated product in gms (glyceride + unsaponifiable matter)	15.39	6.91	12.41	28.05	28.16	9.46
Weight of unsaponifiable matter	0.21	0.10	0.16	0.41	0.43	0.12
Weight percent of glycerides (free from unsaponifiable matter)	15.34	6.88	12.38	27.94	28.03	9.43
Mol percent of mixed acids	15.39	6.84	12.27	28.04	28.06	9.40
Saponification equivalent of liberated acids	280.30	283.20	283.90	280.30	281.00	282.40
Iodine value of liberated acids (Hanus)	157.10	125.30	92.12	129.60	135.10	60.95
Thiocyanogen value of liberated acids (24 hours)	96.26	62.53	61.06	90.33	90.10	60.75
Saponification equivalent of saturated acids obtained on oxidation		289.10	284.20			287.90

TABLE 11  
Mol percent of acids in each fraction

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>
Mol percent of mixed acids	15.39	6.84	12.27	28.04	28.06	9.40
Linolenic acid	6.54	—	—	—	—	—
Linoleic acid	65.42	69.96	34.52	43.47	49.94	—
Oleic acid	28.04	—	33.36	56.53	50.06	67.80
Saturated acids	—	30.04	32.12	—	—	32.20

TABLE 12  
Mol percent of acids on total acids

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	mean
Linolenic	1.00	—	—	—	—	—	1.00 (1.04)
Linoleic	10.07	4.78	4.24	12.19	14.02	—	45.30 (46.42)
Oleic	4.32	—	4.09	15.85	14.04	6.37	44.67 (44.38)
Saturated	—	2.06	3.94	—	—	3.03	9.03 (8.20)

The results obtained above are in fair agreement with those obtained for the component fatty acids of the oil which are also given (mol percent) in the above table in brackets for comparison.

From the above figures the probable component glycerides of the oil of *Sphaeranthus indicus* have been calculated as shown below (Table 13):—

TABLE 13  
Probable component glycerides of the oil of *Sphaeranthus indicus* (Mol percent)

Glycerides in	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	Mean
	15.39	6.84	12.27	28.04	28.06	9.40	100
1 Fully saturated glycerides	Nil	Nil	Nil	Nil	Nil	Nil	
2 Disaturated glycerides	Nil	Nil	Nil	Nil	Nil	Nil	
3 Monosaturated glycerides							
(a) Saturated dilinolein		6.18					6.18
(b) Saturated oleolinolein			11.82				11.82
(c) Saturated diolein						9.09	9.09
4 Triunsaturated glycerides—							
(a) Linoleoleolinolein	3.00						3.00
(b) Trilinolein	2.43	0.66					3.09
(c) Oleodilinolein	9.96		0.45	8.53	14.00		32.94
(d) Dioleolinolein				19.51	14.06		33.57
(e) Triolein						0.31	0.31

In these calculations all the saturated acids have been considered as one acid. Also as all the saturated acids of the oil of *Sphaeranthus indicus* are combined as monosaturated diunsaturated glycerides, we can assume that they are proportionally distributed in monosaturated dilinolein, monosaturated oleolinolein and monosaturated diolein. From the above considerations the component glycerides of the oil of *Sphaeranthus indicus* may be given as follows — palmitodilinolein (0.8%), stearodilinolein (4.1%), arachidodilinolein (1.3%), palmitooleolinolein (1.5%), stearooleolinolein (7.9%), arachidooleolinolein (2.5%), palmitodiolein (1.1%), steardiolein (6.0%), arachidodiolein (1.9%), linoleooleolinolein (3%), trilinolein (3.1%), oleodilinolein (32.9%), dioleolinolein (33.6%) and triolein (0.3%).

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# THE EFFECT OF H-ION CONCENTRATION ON THE TIME OF SETTING AND VISCOSITY CHANGES DURING THE SETTING OF THORIUM ARSENATE GEL-FORMING MIXTURES

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The changes in pH caused by the addition of different amounts of HCl to mixtures giving rise to thorium arsenate gels have been discussed and their effect on the time of setting and the increase in viscosity during setting has been brought out. It has been found that the time of setting of a gel-forming mixture is minimum when its pH is maximum, also a reversal in the increase in viscosity during setting takes place at maximum pH.

The effect of H-ion concentration on the time of setting of gels has been most exhaustively and systematically studied in the case of gels of silicic acid by Hurd and co-workers (cf. Hurd and Carver, *J. Phys. Chem.*, 1933, 37, 321, Hurd and Miller, *ibid* 1934, 38, 668). Hurd and Paton (*J. Phys. Chem.*, 1940, 44, 57) have confirmed in a remarkable manner, the specific effect of H-ion concentration on the time of setting of silicic acid gels. On adding the same amount of extra acetic acid to the same silicic acid gel-forming mixture at different intervals from the commencement of the formation of the gel, they have shown that the setting of the gel proceeds at the same rate as without the addition of the extra acid, for the time before the acid is added, and subsequently at the rate followed in the presence of the extra acid added at the commencement of the setting.

Very little work has been done on the effect of H-ion concentration on the time of setting of other gels. The only early reference available in the literature is the observation of Freundlich and Sollner (*Koll. Zeit.*, 1928, 44, 309, 45, 348) who found that the time of setting of iron hydroxide gel increases from 82 seconds to 9000 seconds when the pH of the gel-forming system is changed from 3.86 to 3.11. Recently Prasad and Desai (*J. Univ. Bom.*, 1938, 7, 132) measured the time of setting and the pH

of some mixtures giving rise to several inorganic gels. They found that there is no definite relationship between the  $pH$  and the time of setting. For example, in the case of stannic phosphate gels, the time of setting decreases and so does the  $pH$  on increasing the amount of phosphoric acid (the constituent I containing the anion of the gel-forming substance) in the mixture, but on increasing the amount of stannic chloride (the constituent II containing the cation of the gel-forming substance), the time of setting increases while the  $pH$  decreases. Same observations have been made on increasing the amounts of the constituents I and II in mixtures giving rise to gels of stannic, manganese and zinc arsenate and of ceric phosphate. In gels of thorium arsenate and thorium phosphate the above mentioned observations have been found to hold with regard to constituent I only, with an increase in the amount of thorium nitrate in the mixture no change in  $pH$  has been observed while the time of setting first decreases and then increases in the former case and regularly increases in the latter. In the case of gels of thorium molybdate they found that with the addition of increasing amounts of  $HCl$  to a gel-forming mixture the  $pH$  decreases continuously, while the time of setting decreases and increases in succession. They further found that no change in  $pH$  takes place during the gelation of all the gels studied by them.

A systematic work on the relation between the time of setting and  $H$ -ion concentration has been carried out by Miss Nathan (J. Indian Chem. Soc., 1943, 20, 159) (in the case of thorium phosphate gels, the  $pH$  of a gel-forming mixture was changed by the addition of varying amounts of  $HCl$  to the mixture). She found that with a continuous decrease in  $pH$  the time of setting of the several gel-forming mixtures first decreases and then increases, and the minimum time of setting occurs at lower  $pH$ , smaller the concentration of phosphoric acid in the mixture. She found no linear relation between  $pH$  and logarithm of the time of setting as observed by Hurd and co-workers (loc. cit.). She also observed no change in the  $pH$  of the gel-forming mixtures either on standing or on the addition of different amounts of alcohol. Further she found that the mixtures set to a gel only when their  $pH$  values are less than 1.7, if this value is exceeded a precipitate and not a gel is formed.

In the present investigation an attempt has been made to study systematically the relation between the  $pH$  and the time of setting of thorium arsenate gel-forming mixtures, the  $pH$  was altered by the addition of different

amounts of  $HCl$ . These gels are particularly interesting because they are clear or translucent when just set and become translucent or opaque, respectively, on standing.

Miss Nathan (J. Indian Chem. Soc., 1943, 20, 56) has also found that the viscosity changes taking place in thorium phosphate gel-forming mixtures with time are a function of its  $pH$ . She found that increase in viscosity with time takes place more rapidly as the  $pH$  of the mixtures is reduced up to a certain value, further reduction in  $pH$  lowers down the rate of increase in viscosity. The effect of  $pH$  on the increase of viscosity with time of thorium arsenate gel-forming mixtures was therefore, also studied in this investigation. The viscosity changes during the setting of these gels have been measured by Prasad and Shejwalkar (J. Indian Chem. Soc., 1940, 17, 508) who have examined the effects of the change of concentrations of the constituents of the gel-forming mixture and of temperature and of the addition of non-electrolytes and electrolytes ( $NaCl$  and  $BaCl_2$ ) to several mixtures.

#### EXPERIMENTAL

##### *Time of Setting*

Hurd and Letteron's method described by Miss Nathan (loc. cit.) was employed for the measurement of the time of setting. All the observations were taken at  $35^\circ$ . Glass rods of 0.094 cms and 0.062 cms diameters were, respectively, used for the results given in the first two and the third tables. The rod of smaller diameter had to be used in the latter case as the gels formed were not firm enough to support the rod of the bigger diameter.

##### *pH*

The  $pH$  of the various gel-forming mixtures was measured by the quinhydrone method on Student Potentiometer, which was tested, using potassium hydrogen phthalate buffer ( $pH=3.97$ ), every time a set of observations was taken. For this purpose the two constituents of the gel-forming mixtures were separately saturated with solid quinhydrone and kept overnight and were mixed when the readings were taken.

##### *Solutions*

Following solutions were used for the preparation of gels

- (1) 6 per cent ( $N/2$ ) solution of thorium nitrate prepared from Kahlbaum's pure chemical,

- (ii) 10 per cent solution of arsenic acid prepared from Merck's pure pyro-arsenic acid,  
 (iii) 2N HCl

### Experimental Procedure for Time of Setting

A known volume of thorium nitrate solution was taken in one test tube and in the other were taken different volumes of the arsenic acid solution with the requisite amount of HCl solution and distilled water so that the total volume on mixing was 10 c.c. The two test-tubes were kept in the thermostat for half an hour and then the two solutions were mixed by pouring the contents of one into the other, five times over. The mixture was then placed in the weighing bottle wherein it was allowed to set, with the glass rod inserted in it in accordance with the requirements of the above named method for the determination of the time of setting.

### Results

The results obtained are given in Tables I, II and III in which X represents the c.c. of arsenic acid solution in the mixture and T the time of setting in minutes. The results are a mean of several readings which did not differ from each other by more than 2.5 seconds and were taken by shifting the rod only when the gel was about to set.

TABLE I  
 Thorium Nitrate = 5 c.c.

HCl c.c.	X = 0.45		X = 0.50		X = 0.55		X = 0.60	
	T	pH	T	pH	T	pH	T	pH
0.00		1.25		1.17	140.0	1.15	90.0	0.92
0.05		1.29	110.0	1.22	65.0	1.19	33.5	0.97
0.10	111.0	1.32	66.5	1.25	20.0	1.21	14.0	1.02
0.15	86.0	1.35	48.0	1.29	15.0	1.25	8.5	1.05
0.25	31.0	1.93	16.75	1.32	6.5	1.27	5.0	1.09
0.40	17.0	1.44	6.25	1.35	5.0	1.29	2.0	1.15
0.60	24.0	1.31	10.0	1.23	6.0	1.19	2.5	1.11
0.80	41.5	1.09	19.0	0.97	8.0	0.95	3.75	0.95
1.00	67.5	0.99	29.0	0.92	10.5	0.92	5.5	0.90

TABLE II  
Thorium Nitrate = 6 c c

HCl c c	X = 0.45		X = 0.50		X = 0.55		X = 0.60	
	T	pH	T	pH	T	pH	T	pH
0.00		1.54		1.19	142.0	1.07	108.0	0.84
0.05		1.75	120.0	1.25	52.0	1.25	38.0	1.07
0.10	135.0	1.95	78.0	1.72	32.0	1.45	27.0	1.30
0.15	69.0	2.33	53.0	1.80	21.0	1.57	16.0	1.34
0.25	40.0	2.45	25.0	1.96	15.0	1.77	9.0	1.40
0.40	23.0	2.69	21.0	2.19	11.0	1.80	6.0	1.55
0.60	33.0	2.51	26.0	2.04	16.5	1.71	8.0	1.39
0.80	46.0	2.29	34.0	1.85	20.0	1.57	12.0	1.17
1.00	77.0	2.01	45.0	1.35	28.0	1.24	18.25	1.04

TABLE III  
Thorium Nitrate = 7 c c

HCl c c	X = 0.45		X = 0.50		X = 0.55		X = 0.60	
	T	pH	T	pH	T	pH	T	pH
0.00		2.54		1.85		1.64		1.44
0.05		2.92		2.17		1.80		1.52
0.10		3.30		2.55	140.0	2.14	110.0	1.64
0.15		3.40	135.0	3.09	100.0	2.39	52.5	1.94
0.25	101.0	3.52	70.0	3.40	52.0	2.65	29.0	2.03
0.40	60.0	3.60	54.0	3.57	34.0	2.80	13.75	2.30
0.60	65.0	2.57	58.0	3.02	41.0	2.37	19.0	1.97
0.80	75.0	2.14	63.0	2.49	50.0	2.09	28.0	1.42
1.00	95.5	2.02	74.0	1.97	63.0	1.80	34.0	0.95

### Viscosity Measurements

Scarpa's method employed by Prasad and Modak (Proc Ind Acad Sci, 1940, 11, 282) was used for this purpose. The diameter and the length of the capillary tube were 0.0995 cms and 4.395 cms, respectively, and the volume of the bulb between the two marks was 1.72 c c. The pressure applied for suction was 16 cms. of water and was kept constant throughout. The constant of the apparatus was found to be 0.00165. All the measurements were taken at 35°.

The concentrations of the solutions used were the same as mentioned before.

The chosen constituents of a gel-forming mixture were mixed in the same manner as described in the foregoing pages and the mixture was

poured in the viscosity bottle. The times of rise and fall of the gel-forming mixture between the fixed marks on the viscometer were measured after known intervals of time  $t$  (expressed in minutes), from the time of mixing and the results obtained are shown graphically in figs 1 and 2 in which viscosity (expressed in millipoises) is plotted against  $t$ . The readings were continued in each case until the mixture would not rise and fall through the capillary in reasonable time.

### DISCUSSION OF RESULTS

It will be seen from the results given in tables I, II and III that with the addition of increasing amounts of hydrochloric acid the time of setting of all gel-forming mixtures first decreases, reaches a minimum, and then increases. The minimum, in all cases, has been found to take place in the presence of 0.40 c.c. of the  $HCl$  solution. With the similar addition of the acid the  $pH$  first increases, reaches a maximum value and then decreases, the maximum  $pH$  has been observed with mixtures containing 0.40 c.c. of the  $HCl$  solution, that is, those which set in minimum time. However, it will be noticed from these tables that the  $pH$  of various mixtures setting in minimum time has no fixed value.

On plotting the  $pH$  values against the logarithm of the time of setting two intersecting straight lines are obtained. These are shown in Fig. 3, for mixtures containing 5.0 c.c. of thorium nitrate and 0.45, 0.50, 0.55 and 0.60 c.c. of arsenic acid solution. Similar lines are obtained for other mixtures used in this investigation, the intersecting point in each case corresponding to the mixture which sets in minimum time.<sup>\*</sup> These observations are different from those made on gels of thorium phosphate.

It was found that the  $pH$  of the solution obtained by diluting 5.0 c.c. of the solution of thorium nitrate to 10.0 c.c. by the addition of distilled water is 2.39. The  $pH$  values of solutions obtained by diluting 0.45 c.c. and 0.60 c.c. of the solution of arsenic acid to 10.0 c.c. by the addition of distilled water were found to be, respectively, 1.88 and 1.17. The  $pH$  values of the gel-forming mixtures containing 5.0 c.c. of thorium nitrate and 0.45 and 0.60 c.c. of arsenic acid solution, made up to 10.0 c.c., are 1.25 and 0.92, respectively. This shows that the formation of thorium arsenate is followed by a decrease in  $pH$ , probably on account of the nitric acid formed in the reaction between the constituents of the gel-forming mixture.

While preparing the gels it was observed that when solutions of thorium nitrate and arsenic acid are mixed, a precipitate is obtained which is reduced first to a finely divided state and then disappears extremely slowly during the transference of the contents of one test tube into another. It was found that the finely divided precipitate was present in some gel-forming mixture even after the gel had set, and disappeared only after keeping the gel for some time. For a time, the gel was clear but later it developed a turbidity which increased enormously until the whole gel became opaque.

With the addition of increasing amount of  $HCl$  to the gel-forming mixture it was observed that the precipitate disappeared more quickly and in the presence of large amounts of  $HCl$  it did not appear at all. Thus the action of  $HCl$  in these mixtures is that of peptisation and hence it is opposed to the action which causes precipitation. Since the precipitation of thorium arsenate is accompanied by a decrease in  $pH$ , it is clear from the above arguments that the peptisation would be followed by an increase in  $pH$ . This has actually been observed. The optimum conditions reached in all cases in the presence of 0.4 c.c. of the  $HCl$  solution. The decrease in  $pH$  on the addition of amounts of  $HCl$  greater than 0.4 c.c. seems to be a normal effect.

If the density of charge on the micelles in the gel-forming mixtures is assumed to be due to the adsorption of  $H$ -ions from the medium, then it would decrease with an increase in the amounts of  $HCl$  upto 0.4 c.c. and would begin to increase with the addition of larger amounts of  $HCl$ .

It will appear from the above discussion that two types of gels are obtained, one from mixtures containing 0.0-0.4 c.c. of  $HCl$  and the other from those containing more than 0.4 c.c. of the acid. The character of these two types of gels has also been found to be different. The latter gels become dead opaque on standing and do not synerise, while the former do not become so opaque on standing and exhibit syneresis. Also the texture of the latter gel-forming mixtures during the course of gel-formation is fairly loose.

It will be seen from the above tables that the time of setting and the  $pH$  values of all mixtures containing the same amounts of arsenic and hydrochloric acids increase as the amount of thorium nitrate in them is increased. Thorium ions are well known as peptising agents and hence their increase in a gel-forming mixture would cause the same effect as the addition of  $HCl$  upto 0.4 c.c., that is, an increase in  $pH$ , as observed.

It would appear from the above discussion that the peptisation of thorium arsenate in the gel-forming mixture containing no  $HCl$  is brought about by (i)  $H$ -ions present in the mixture and (ii) thorium ions which have not entered into reaction with arsenic acid. Since the amounts of these peptising ions are not sufficiently large, the peptisation does not take place to a great extent and hence some precipitate remains unpeptised even after the gel sets, as mentioned before.

It will be noticed from the curves in figure 3 that the time of setting of thorium arsenate gels is not a function of  $pH$  only. Mixtures containing the same amount of thorium nitrate and having the same  $pH$  take different time to set if the amounts of arsenic and hydrochloric acids in the mixture are changed.

It will be seen from the foregoing tables that (i) the time of setting and (ii) the  $pH$  of a mixture (including the one setting in minimum time) containing the same amounts of solutions of thorium nitrate and  $HCl$  decrease as the amount of arsenic acid in the mixture is increased. The decrease in the time of setting in the presence of larger amounts of arsenic acid may be due to a slight increase in the amount of the gel-forming substance in the colloidal state. It will be found from the volumes and the concentrations of solutions of thorium nitrate and arsenic acid used in this investigation that in all cases thorium nitrate is in good excess. Tables I, II and III also bring out clearly that the same value of  $pH$  is reached in the presence of greater amount of  $HCl$  when increased amounts of arsenic acid are used. This happens probably because larger amounts of  $HCl$  are required to peptise greater amounts of the gel-forming substance formed under the circumstances. It is a surprising coincidence that the maximum value of  $pH$  in all cases is reached in the presence of 0.4 c.c. of  $HCl$ . It is, however, probable that the changes in the time of setting are caused by the changes in the structure of gels formed in the presence of different amounts of arsenic acid owing to the differences in the rate of their formation.

The decrease in  $pH$  mentioned above may be due to an increase in the amount of (i) arsenic acid and (ii) nitric acid formed in the reaction between arsenic acid and thorium nitrate, in case there is an increase in the micellar content of the gel-forming mixture. The former explanation is supported from the data given in the first row of the tables I, II and III which show that the  $pH$  of the gel-forming mixtures containing no  $HCl$  decreases as the amount of arsenic acid in the mixture is increased.



On the addition of methyl and ethyl alcohols and glycerine to some of the gel-forming mixtures, corresponding to the two types of gels, that is, those containing larger and smaller amounts of  $HCl$  than that of the mixture setting in the minimum time, it was found that the time of setting increases as larger amounts of the non-electrolytes are added. The time of setting was found to be too great in the presence of large amounts of alcohols and also the gels formed were loosely set. No change in the  $pH$  of any gel-forming mixture was observed on the addition of alcohols. This observation is similar to that made by Miss Nathan and leads to the conclusion that the addition of alcohols to thorium arsenate gel-forming mixtures only decreases the rate of gel-formation.

The curves in figures 1 and 2 show that the increase in viscosity of a gel-forming mixture during setting changes with the addition of different amounts of (i)  $HCl$ , that is, with a change in  $pH$ , and (ii) thorium nitrate. It will be observed that in the case of the mixture containing 5.0 c.c. of thorium nitrate the viscosity-time curves rise slowly in the early stages of gelation and rapidly in the subsequent ones and the increase in viscosity becomes more and more rapid as the  $pH$  is increased (cf. Fig. 1). However, in mixtures containing 7.0 c.c. of thorium nitrate the viscosity-time curves are S-shaped and the rate of change of viscosity increases with an increase in  $pH$  upto 3.40 and then decreases. Probably this reversal in viscosity changes corresponds to the minimum time of setting. No such reversal could be observed with the mixtures containing 5.0 c.c. of thorium nitrate because flakes separate out when more than 0.2 c.c. of  $HCl$  are added to it and no viscosity measurements could be possibly taken.

Several workers have pointed out that an increased rate of change of viscosity during gelation is due to the low density of charge on the micelles and greater degree of hydration. If these conclusions be adopted then they confirm the observations made above that the addition of  $HCl$  before the minimum setting condition decreases the density of charge on the micelles.

The authors feel grateful to Dr. Mata Prasad, D.Sc., F.I.C., for suggesting the problem and the guidance throughout the progress of this work. One of the authors (SSB) is also thankful to Mr. M. B. Kabadi, M.Sc., for his guidance and help.

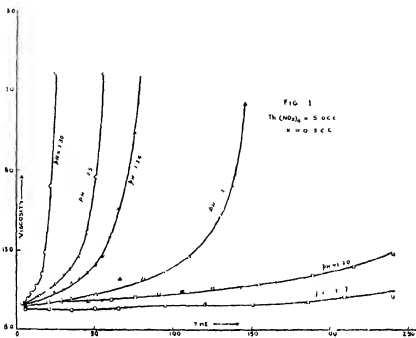
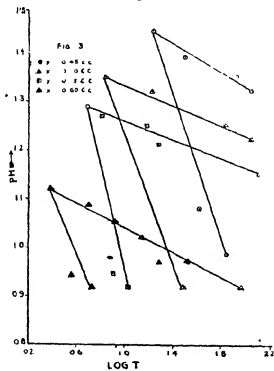


Fig 1



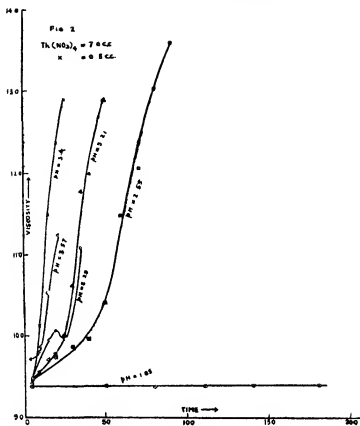


Fig 3

## CHEMICAL EXAMINATION OF *CASSIA ALATA* LINN. PART I. THE COMPONENT ACIDS OF THE FATTY OIL FROM THE SEEDS

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The seeds of *Cassia alata* Linn. yield 5.02% of a non-drying clear yellow fatty oil having  $d_{40}^{20}$  0.8898,  $n_D^{20}$  1.4681, acid value 9.15, sap value 165.4, acetyl value 13.65, Hehner value 83.86, R. M. 0.08, unsaponifiable matter 4.41%,<sup>1</sup> iodine value (Hanus) 91.28 and thiocyanogen value (24 hours) 63.82.

The component fatty acids of the oil were found to be linoleic 37.81%, oleic 37.33%, palmitic 9.90% and lignoceric 14.96%. The unsaponifiable matter consisted of a sitosterol, phytosterol, M. P. 133–134°C besides a small amount of a colouring matter.

*Cassia alata* Linn. commonly known as ringworm shrub in English, Dadmurdan in Hindi and Dadrughna in Sanskrit belongs to the natural order Leguminosae. It grows in abundance in Bengal and also in other parts of India.

According to Dey,<sup>1</sup> Kirtikar and Basu,<sup>2</sup> Dymock, Warden and Hooper,<sup>3</sup> the plant has been described to be highly medicinal in the indigenous system of medicine. One of the native names of the plant is derived from its efficacy in curing ringworm. The leaves of the plant are commonly used in itching, ringworm, skin diseases, coughs and asthma and also as expectorant and purgative.

In spite of the reputed medicinal value of the plant, no work has been done on its chemical examination. Only the fatty oil from a few other allied species of the genus has been examined. Jois and Manjunath<sup>4</sup> have examined the fatty oil from the seeds of *Cassia tora* and reported the presence of linoleic, oleic, palmitic and lignoceric acids. Ahmad<sup>5</sup> examined the fatty oil from *Cassia absus* and showed that the component fatty acids consisted of oleic, linoleic, palmitic, stearic and lignoceric acids. Steger and Van Loon<sup>6</sup> reported the presence of oleic, linoleic, linolenic, palmitic and stearic acids in the fatty oil of *Cassia occidentalis*. The physical and che-

mical constants of the fatty oils from allied species, as reported by above workers, are given in table 1 along with our results for comparison. As no work has been done on *Cassia alata*, it was thought desirable that a systematic chemical examination of the plant would be interesting and useful and with this object the present work was undertaken. In the present communication the results of the examination of the fatty oil from the seeds of *Cassia alata* are reported. Further work on the seeds and other parts of the plant is in progress and will be reported later.

As a result of our examination we find that the fatty acids from the oil of *Cassia alata* consist of linoleic (37.81%), oleic (37.33%), palmitic (9.90%) and lignoceric (14.96%) acids. No linolenic or stearic acid has been found. Thus the fatty acid composition of the oil of *Cassia alata* resembles that of the oil of *Cassia tora* and differs from that of *Cassia absus* or *Cassia occidentalis*. Further a comparison of the physical and chemical constants of the oils from allied species as given in table 1 shows that the constants of the oil of *Cassia alata* resemble those of *Cassia tora* and differ considerably from those of *Cassia absus*. Thus for example the iodine value of the oil from *Cassia alata* is 91.28, that of *Cassia tora* is 90.7, but that of *Cassia absus* is 130.5. Looked at from this point of view the oils of *Cassia alata* and *Cassia tora* will be classed as non-drying oils, whereas the oil of *Cassia absus* will be classed as a semi-drying oil almost approaching to a drying oil. The above mentioned chemical composition of the fatty acids shows that the oil of *Cassia alata* resembles other leguminosae seed fats in conforming to the simple "linoleic-oleic-palmitic" type, the chief components linoleic and oleic acids form about 75% of the total component acids. A reference should, however, be made to lignoceric acid which is present to the extent of about 15%, as the melting point of the isolated acid is lower than that of *n*-tetracosanic acid (84°C). Previously it was thought that the plant acid may be a branched chain acid with lower melting point. From later work, especially on the evidence of X-ray spectra<sup>12</sup> it seems likely that the natural lignoceric acid is a normal chain one and the lower melting point observed may in some cases be influenced by the presence of small amounts of some other acid contaminating the main acid. Ours is not an isolated observation as other workers<sup>13</sup> have found in seed oils lignoceric acid with lower melting point ranging from 75°C to 78°C.

Another interesting feature regarding these oils is the high percentage

of the unsaponifiable matter which in the case of the oil of *Cassia alata* has been found to consist mostly of a phytosterol, sitosterol, M P 133-34°C and a small amount of the colouring matter

### EXPERIMENTAL

Two kilogrammes of the powdered seeds were extracted with petroleum ether (40-60°C) in a five litre extraction flask. On distilling off the solvent about 100 gms of an yellow brown oil, having a characteristic odour, were obtained. As more petroleum ether was not available, another lot of three kilogrammes was extracted with carbon tetrachloride in two instalments. On distilling off the solvent and leaving the oil overnight, an orange coloured solid separated which was filtered off. No solid, however, separated from the oil extracted with petroleum ether. The two samples of the oil were then purified with animal charcoal and Fuller's earth whereby clear golden yellow coloured oils were obtained. The saponification and iodine values of the two oils were found to be in fair agreement within experimental error (S V 165.4, I V 91.28 in petroleum ether and S V 163.4 and I V 89.99 in carbon tetrachloride). The two samples of oils were, therefore, mixed and examined. It was found to be a non-drying oil having the following physical and chemical constants (Table I). The constants of the oils from the seeds of allied species are also given for comparison.

TABLE I

	<i>Cassia alata</i>	<i>Cassia tora</i> <sup>4</sup>	<i>Cassia absus</i> <sup>4</sup>
Specific gravity	at 30°C 0.8898	at 25°C 0.8969	0.9272
Refractive index	at 25°C 1.4681	at 25°C 1.4669	1.4840
Acid value	9.15	10.8	2.5 <sup>1</sup>
Saponification value	165.4	154.2	190.4
Acetyl value	13.65	9.6	12.0
Hehner value	83.86	78.5	
R M value	0.08	0.15	
Unsaponifiable matter	4.41%	5.4%	8.4%
Iodine value (Hanus)	91.28	90.7	130.5
Thiocyanogen value (24 hours)	63.82		

Two hundred and twenty-five grammes of the oil were then saponified with an alcoholic solution of sodium hydroxide, the unsaponifiable matter removed with ether and the soap solution decomposed with dilute sulphu-

ric acid when fatty acids (175 gms.) having the following characteristics were obtained (Table 2):—

TABLE 2

Consistency	liquid (solidified on keeping)
Neutralisation value	198.3
Saponification equivalent	283.0
Iodine value (Hanus)	105.1
Thiocyanogen value (24 hours)	70.1

The fatty acids were then separated into solid and liquid acids by Twitchell's Lead Salt-Alcohol process.<sup>7</sup> The percentage, the iodine and thiocyanogen values, the neutralisation values and the saponification equivalents of the solid and liquid acids are recorded below (Table 3) —

TABLE 3

Acids	%	Iodine value	Thiocyanogen value	Neutralisation value	Saponification equivalent
Solid	24.85	183	—	192.9	290.9
Liquid	75.15	134.90	89.48	201.1	279.0

### EXAMINATION OF THE LIQUID ACIDS

The liquid acids were oxidised with a dilute solution of alkaline potassium permanganate according to the method of Lapworth and Mottram<sup>8</sup> when a dihydroxy stearic acid M P 133°C and a tetrahydroxy stearic acid M P 170°C were obtained showing the presence of oleic and linoleic acids only.

The two acids were quantitatively determined by brominating the liquid acids in ether solution at -10°C according to the method of Eibner and Muggentholar<sup>9</sup> modified by Jamieson and Boughmann.<sup>10</sup> The results of bromination and analysis are given below (Table 4) —

TABLE 4

Weight of liquid acids	-7.8736 gms.
Weight of linoleic tetrabromide	-6.5446 gms.
Melting point of linoleic tetrabromide	-113.5°C
Weight of the residue (tetra-+di-bromide)	-7.9815 gms
Bromine contents of the residue (Piria and Schiff's method)	-40.24%

Weight of linoleic tetrabromide in the residue	- 1 8905 gms
Weight of oleic di-bromide in the residue	- 6 0910 gms
Total weight of linoleic tetrabromide	- 8 4351 gms
Weight of linoleic acid	- 3 9372 gms
Weight of oleic acid	- 3 8866 gms

From the above results the percentages of linoleic and oleic acids in liquid acids, in mixed acids and in the oil have been calculated and are given below (Table 5).—

TABLE 5

Acids	Percentage in liquid acids	Percentage in mixed acids	Percentage in oil
Linoleic	50.32 (50.14)	37.81	31.71
Oleic	49.68 (49.00)	37.33	31.30

The figures in brackets are those calculated from the Thiocyanogen value of the liquid acids (vide Table 3)

The calculated iodine value of a mixture of 50.32% linoleic and 49.68% oleic acid is 135.79 which is in good agreement with the iodine value of liquid acids (Table 3). The percentages of these two acids in mixed acids were also calculated from the thiocyanogen and iodine values of mixed acids. These results are given below (Table 6) for comparison with those obtained by bromination of liquid acids.

TABLE 6

Acids	Percentage by bromine addition method	Percentage by calculation from thiocyanogen and iodine values
Linoleic	37.81	38.64
Oleic	37.33	39.03

### EXAMINATION OF SOLID ACIDS

The solid acids were first rubbed over a porous plate to free them from any liquid acids and they were then found to melt at 55°C. They were then converted into methyl esters which were distilled under reduced pressure (Table 7).



TABLE 7

Weight of esters distilled 33.96 gms

Fraction No	Pressure	Temperature range	Weight in grammes
1	10 mm	upto 165°C	7.87
2	10 mm	165-170°C	6.99
3	10 mm	170-175°C	5.63
4	10 mm	175-185°C	4.94
5	10 mm	185-190°C	5.32
6 (Residue)			2.80

The saponification value, the saponification equivalent and the iodine values of all the fractions were determined and the amounts of various acids in different fractions were calculated according to the method of Jamieson and Boughmann<sup>11</sup> (Table 8) —

TABLE 8

Fraction No	Iodine value	Saponification value	Saponification equivalent	Palmitic acid		Lignoceric acid		Unsaturated acids	
				%	gms	%	gms	%	gms.
1.	1.02	186.3	301.1	67.92	5.346	26.54	2.088	0.76	0.060
2	1.35	177.0	316.9	54.19	3.787	40.25	2.814	1.00	0.070
3	1.49	165.0	340.0	54.47	1.941	60.19	3.388	1.11	0.063
4	1.63	154.2	363.8	14.22	0.703	80.63	3.983	1.21	0.060
5	1.89	149.6	375.0	4.58	0.243	90.24	4.800	1.40	0.075
6. { Unpolymerised (1.17 gms) Residue	2.50	128.3	437.3			94.43	1.105	1.85	0.022
6. { Polymerised (1.26 gms)									
TOTAL					12.020		18.178		0.350

*Fraction 1.* The acids obtained after saponification of the fraction melted at 56°C. On repeatedly crystallising the acids from acetone, palmitic acid M.P. 61°C was obtained, the identity of which was established by the determination of mixed melting point with an authentic sample of palmitic acid when no depression was observed. The filtrate gave an acid of lower melting point 58-59°C which rose on the addition of pure palmitic acid but was depressed with stearic acid and myristic acid.

*Fractions 2, 3 and 4.* The liberated acids from these fractions on repeated crystallisation from dilute acetone gave acids with M.P.  $64-65^{\circ}\text{C}$  which were depressed with pure palmitic and stearic acids, showing that they are not stearic acid. From the mother liquor, however, palmitic acid M.P.  $61^{\circ}\text{C}$  could be isolated and this was not depressed with an authentic sample of palmitic acid.

*Fraction 5.* The acid M.P.  $59^{\circ}\text{C}$  was repeatedly crystallised from acetone but the melting point did not rise above  $64^{\circ}\text{C}$ . In order to effect the separation of the high molecular weight acid, magnesium salts were prepared and from the least soluble portion an acid was obtained which on repeated crystallisation melted at  $74-75^{\circ}\text{C}$ . The melting point was depressed by the addition of pure palmitic and arachidic acids showing that the acid is not arachidic. This acid was again converted into magnesium salt and from the least soluble part an acid M.P.  $75-76^{\circ}\text{C}$  was obtained which was also depressed with arachidic acid.

From the most soluble magnesium salts, palmitic acid M.P.  $61^{\circ}\text{C}$  was isolated which gave no depression with pure palmitic acid.

*Fraction 6.* The residue was deep coloured; it was saponified and the liberated acids extracted with petroleum ether when an acid M.P.  $67^{\circ}\text{C}$  was obtained. On repeated crystallisation from acetone the melting point rose to  $76^{\circ}\text{C}$  when further crystallisation was not possible. This melting point was depressed by the addition of arachidic acid. The molecular weight of the acid obtained from the residue was 364.8 which agrees with the molecular weight of lignoceric acid.

It is thus clear that only palmitic acid could be isolated. No stearic acid or arachidic acid was obtained from any of the fractions. The other acid besides palmitic that appears to be present is an acid M.P.  $76^{\circ}\text{C}$  and molecular weight 364.8. The molecular weight agrees with that of lignoceric acid, but the melting point is lower than that of lignoceric acid (M.P.  $84^{\circ}\text{C}$ ) and agrees with that of arachidic acid. But on addition of pure arachidic acid the melting point is depressed showing that the acid is not arachidic. The acid must, therefore, be lignoceric. As regards the lower melting point, it may be said that several workers<sup>18</sup> who have isolated lignoceric acid from fatty oils have recorded its melting point ranging from  $75-78^{\circ}\text{C}$ . The saturated acids present in the oil are, therefore, palmitic and lignoceric. It may be also noted that the saturated acids present in the

oil of *Cassia tora* are palmitic and lignoceric, and that lignoceric acid is generally a constituent of the oils of seeds belonging to leguminosae family.

The percentages of various solid acids in mixed solid acids, in mixed acids and in the oil are given below (table 9):

TABLE 9

Acid	Percentage in solid acids	Percentage in mixed acids	Percentage in oil
Palmitic	39.81	9.90	8.30
Lignoceric	60.19	14.96	12.55

#### EXAMINATION OF THE UNSAPONIFIABLE MATTER

The unsaponifiable matter obtained by extracting the soap with ether was an yellow brown mass having a characteristic odour which was also present in the oil. This gave all the colour reactions of phytosterol.

On crystallising it with alcohol, a white substance M.P. 133-34°C was obtained. The mother liquor was orange red in colour and on concentration it gave some more of the above solid. The mother liquor from this consisted mostly of the colouring matter.

This solid gave all the colour reactions of a phytosterol and was identified to be a sitosterol found in most vegetable oils. The acetyl derivative melted at 121°C. The unsaponifiable matter of the oil of *Cassia alata*, therefore, consists of a sitosterol and some colouring matter.

#### Acknowledgment

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# CHEMICAL EXAMINATION OF PINUS GERARDIANA WALL. THE COMPONENT FATTY ACIDS AND THE PROBABLE GLYCERIDE STRUCTURE OF THE FATTY OIL FROM THE SEEDS.

By BAWA KARTAR SINGH AND RAM DAS TIWARI

[From the Department of Chemistry, Allahabad University, Allahabad], Received on 6-9-43

The fatty oil from the seeds of *Pinus gerardiana* Wall has been examined and found to have sp gr 0.9198 (30°C), refractive index 1.4699 (25°C), acid value 1.15, sap. value 191.9, acetyl value 3.7, Hehner value 95.34, unsaponifiable matter 0.64%, R. M 0.215, R. P 0, Iodine value (Hanus) 120.3 and Thiocyanogen value (24 hours) 83.0. The component fatty acids of the oil are linoleic 42.80%, oleic 32.35%, palmitic 3.67% and stearic 1.20%. The unsaponifiable matter consists of a phytosterol, M. P 133°C. The glyceride structure of the oil has been determined by brominating the oil in petroleum ether at -5°C. The component glycerides of the oil are palmitodilinolein 2.41%, steardilinolein 0.78%, palmitooleolinolein 9.86%, steardooleolinolein 3.22%, trilinolein 0.38%, oleodilinolein 32.48%, dioleolinolein 47.45% and triolein 3.42%.

*Pinus gerardiana* Wall is a moderately sized evergreen tree belonging to the natural order Coniferae. The chief product of the tree is the nut sold in the market under the name "Chilgoza". The seeds have been described to be highly medicinal<sup>1,2</sup>. They are appetiser, expectorant, stimulant and carminative. The oil from the seeds is highly estimated for its stimulating and healing power when applied as a dressing to wounds and ulcers. It is applied as an external application in diseases of head.

An analysis of the kernels has been reported by Church<sup>3</sup> and also recently by Hardikar<sup>4</sup>. Grimme<sup>5</sup> has determined the constants of the fatty oil and later Hardikar<sup>4</sup> has examined the oil in detail. He, however, did not examine the solid acids and the unsaponifiable matter. The results obtained by these workers are given along with ours for comparison.

The present investigations were undertaken in order to study the component solid acids, the nature of the unsaponifiable matter and the glyceride structure of the fatty oil.

A detailed examination of the oil has shown that the component fatty acids of the oil are linoleic 42.80%, oleic 52.33%, palmitic 3.67% and stearic 1.20%. The unsaponifiable matter of the oil consists of a phytosterol M.P. 133°C. The results obtained for liquid acids are in fair agreement with those of Hardikar (*loc cit*). It will be thus seen that the fatty acid composition of the seed oil of *Pinus gerardiana* is very similar to that of the other coniferous seeds: the major component acids being oleic (52%) and linoleic (43%), linolenic acid is absent, whereas some coniferous seed oils contain a fairly large amount of this acid. The saturated acids form less than 5% of the total acids, palmitic acid (75% of solid acids) is in very considerable excess over stearic acid (25% of solid acids) as is generally the case with seed fats and oils of coniferous and other large trees.

The component glycerides of the oil were determined by brominating<sup>6, 7, 8, 9, 10</sup> the neutral oil in petroleum ether solution at -5°C, resolving the brominated product into a number of fractions and determining the fatty acid composition of each fraction. As a result of examination the component glycerides of the oil have been found to be palmitodilinolein 2.42%, stearodilinolein 0.78%, palmitooleolinolein 9.86%, stearooleolinolein 3.22%, trilinolein 0.38%, oleodilinolein 32.48%, dioleolinolein 47.45% and triolein 3.42%. These investigations have shown the actual number of glycerides to be 8, whereas the maximum number of individual glycerides which may be obtained by any combination of four different acids with the glycerol radical  $-H_2C-CH-CH_2-$  is 40.

### Experimental

The material employed for the investigation consisted of the authentic seeds of *Pinus gerardiana* obtained from the local market and identified botanically.

The following results were obtained on a preliminary examination of the seeds:—

Average weight of a seed	0.3085 gms.
Percentage of husk	30.2
Percentage of kernel	69.8
Ash content of kernels	3.0%
Moisture content of kernels	8.2%
Percentage of oil in kernels	30.6

A small amount of the crushed kernels was extracted with boiling water. The extract gave no colour with ferric chloride nor did it reduce Fehling's solution, showing the absence of tannins and reducing sugars. It gave blue colour with a dilute solution of iodine, showing the presence of starch. The extract reduced Fehling's solution after hydrolysis with mineral acids, which may be due to the presence of starch or some other polysaccharide. The cold water extract gave no colour with iodine, but reduced Fehling's solution after hydrolysis showing that some other di- or poly-saccharide, besides starch, is also present.

A portion of the crushed kernels was digested with 1% hydrochloric acid for three days. The extract gave no tests for alkaloids.

The ash of the kernels on examination was found to contain the following acidic and basic radicals:—

Water soluble—56%—Chloride, aluminium, sodium and potassium

Water insoluble, (acid soluble)—44%—phosphate, aluminium and calcium

In order to have an approximate idea regarding the solubility of the constituents, 200 gms of the crushed kernels were extracted with a number of solvents in succession with the following results.—

1. *Petroleum ether* (B. P. 40°–60°C)—The extract was yellow in colour which on distilling off the solvent gave a clear yellow fatty oil. Yield 50.6%.

2. *Absolute ether*—Both the extract and residue were similar as in the case of petroleum ether. Yield 1.15%.

3. *Chloroform*—A light yellow coloured extract which left a very small residue was obtained. Yield 5.2%.

4. *Ethyl acetate*—An yellow coloured extract was obtained. Yield 0.35%.

5. *Absolute alcohol*—The alcoholic extract was yellow in colour. The residue gave no test for glucosides or sugars. Yield 1.25%.

6. *Alcohol 70%*—The yellow extract left a residue which gave test for di- or poly-saccharides. Yield 1.4%.

For the purpose of complete examination about five kilograms of the kernels were crushed and the oil was extracted from them by pressing. The yield of the oil of kernels on pressing was about 32%. It was a transparent clear oil having a pale yellow colour.

## Examination of the Fatty Oil

The fatty oil obtained as described above was purified with animal charcoal and Fuller's earth whereby a clear yellow transparent oil was obtained. The physical and chemical constants of this oil were determined. The oil obtained on extracting the kernels with petroleum ether was also purified and its constants determined.

TABLE I

Constants	AUTHOR'S RESULTS		Grimme's results <sup>b</sup>	Hardikar's results <sup>a</sup>
	Solvent— extracted	Pressed		
Specific gravity	0.9198 (30°C)	0.9169 (30°C)	0.9307	0.9144
Refractive Index	1.4699 (25°C)	1.4729 (25°C)		1.4709
Angle of rotation for 2 dcm at 30°C	$\alpha_D = 0.1^\circ$ $\alpha_{4401} = 0.2^\circ$			
Acid value	1.15	3.29	1.6	3.87
Sap value	191.9	192.4	191.3	192.4
Acetyl value	3.7	3.5		4.07
Hehner value	95.34	94.82		95.01
Unsaponifiable Matter	0.64	0.42		0.5
R. M. Value	0.215	0.222		0.33
R. P. Value	0.0	0.0		
Iodine value (Hanus)	120.3	119.7	118.3	121.3
Thiocyanogen value (24 hours)	83.0	83.2		

These results are given in table 1. The results obtained by other workers are also given for comparison.

Eight hundred gramms of the oil was saponified with alcoholic sodium hydroxide, the unsaponifiable matter removed with ether and the fatty acids liberated. The constants of these acids were determined and are given in table 2. The results obtained by other workers are also given for comparison.

TABLE II

Constants	Authors' results	Grimme's <sup>b</sup> results	Hardikar's <sup>a</sup> results
Neutralisation value	200.4	196.77	200.2
Saponification equivalent	280.6	285.2	280.2
Iodine value	124.2 (Hanus)	125.0	127.7
Thiocyanogen value (24 hours)	85.9		



The mixed fatty acids were then separated into solid and liquid acids by Hilditch's modification<sup>11</sup> of Twitchell's<sup>12</sup> lead salt-alcohol process. The neutralisation value, the saponification equivalent, the iodine value and the thiocyanogen value of the solid and liquid components were determined and are given below in table 3.

TABLE III

Constants	Solid acids	Liquid acids
Percentage ..	4.85	95.15
Neutralisation value	208.3	199.6
Saponification equivalent	269.5	281.5
Iodine value (Hanus)	4.0	130.9
Thiocyanogen value (24 hours)	3.0	90.1

### *Examination of the Liquid Acids "*

The liquid acids were first oxidised with a dilute solution of alkaline potassium permanganate according to the method of Lapworth and Mottram<sup>13</sup> when a dihydroxy stearic acid M. P. 132°C and a tetrahydroxy stearic acid M. P. 170°C were obtained, showing the presence of oleic and linoleic acids only in the liquid acids.

A known weight of the liquid acids was brominated<sup>14,15</sup> in ether at -10°C., the results of bromination and analysis are given below in table 4.

TABLE IV

Wt. of acids brominated	..	3.7923 gms.
Wt. of linoleic tetrabromide	.	3.0050 gms.
Melting point of tetrabromide	.	115°C
Wt. of the residue (di-+tetrabromide)	.	3.9255 gms.
Bromine content of the residue (Piria and Schiff's Method)	.	38.45%
Wt. of linoleic tetrabromide in the residue	.	0.6705 gms.
Wt. of oleic dibromide in the residue	..	3.2550 gms.
Total wt. of the tetrabromide	.	3.6755 gms.
Wt. of linoleic acid	..	1.7150 gms.
Wt. of oleic acid	..	2.0750 gms.
Total weight (linoleic+oleic acids)	.	3.7900 gms.
Loss	..	0.0023 gms.
Percentage of linoleic acid in liquid acids	..	45.25
Percentage of oleic acid in liquid acids	.	54.75

The liquid acids were then converted into methyl esters and a known weight of these esters was distilled under reduced pressure. The saponification equivalent and the iodine value of all the fractions were determined. The acids obtained from each fraction after saponification were oxidised with dilute alkaline potassium permanganate when a dihydroxy stearic acid and a tetrahydroxy stearic acid were obtained from each fraction. A small amount of residue in fraction  $L_1$  was left unoxidised which was due to some solid acids that had passed into liquid acids. The amounts of individual acids in each fraction were then calculated as shown in table 5.

TABLE V

Weight of esters distilled 41.50 gms				Pressure 12 m.m			
Fract No	Temp Range	Wt. in gms.	Sap equiv	Iodine value	Methyl oleate	Methyl linoleate	Methyl esters of solid acids
$L_1$	upto 185°C	3.57	294.0	112.8	2.29	1.19	0.08
$L_2$	185-188°C	5.17	295.0	99.9	4.32	0.85	
$L_3$	188-195°C	8.58	295.1	120.9	5.10	3.48	
$L_4$	195-200°C	7.23	294.6	114.7	4.82	2.41	
$L_5$	200-205°C	8.78	295.2	136.8	3.61	5.17	
$L_6$	205-208°C	5.81	295.1	140.7	2.12	3.69	
$L_7$	Residue	2.12	295.4	158.1	0.35	1.77	
Total		41.25	.		22.61	18.56	0.08
Loss in distilling		0.25					.
Hence the composition of liquid acids is—Oleic acid 54.66% Linoleic acid 45.16% Solid acids 0.20%							

The percentages of oleic, linoleic and solid acids in mixed acids were calculated from the thiocyanogen value and iodine value of mixed acids. The exact composition of solid and liquid acids was also calculated from the thiocyanogen and iodine values of the two acids and from these the corrected percentages of oleic, linoleic and solid acids in mixed acids were calculated. The results so obtained are given below (table 6) for comparison with those obtained by other methods and also with those obtained by Hardikar (*loc. cit.*).

TABLE VI

Methods	Oleic acid	Linoleic acid	Solid acids
1 Calculated from SCN value of mixed acids	52.93	42.23	4.79
2 Calculated from SCN value of liquid and solid acids	52.28	42.90	4.82
3 By bromination of liquid acids	52.10	43.05	4.85
4 By methyl ester distillation	51.99	42.97	5.04
5 By Bertram's oxidation method			4.92
Average of 1 to 4	52.33	42.80	4.88
Hardikar's results	54.39	40.69	4.92

A comparison of results obtained by different methods shows that there is a good agreement. For the purpose of calculations the mean of all the results has been taken. Also the results are in fair agreement with those of Hardikar (*loc cit.*)

#### Examination of solid acids

The solid acids were converted into methyl esters. 29.85 gms of esters were distilled fractionally under reduced pressure, and the results of distillation and calculation<sup>16</sup> are given in tables 7 and 8.

TABLE VII

Fract. No	Pressure	Temperature range	Wt. in gms
S <sub>1</sub>	11 m.m.	170-175°C	6.10
S <sub>2</sub>	11 m.m.	175-178°C	9.84
S <sub>3</sub>	11 m.m.	178-180°C	3.80
S <sub>4</sub>	11 m.m.	180-185°C	5.28
S <sub>5</sub>	11 m.m.	185-190°C	2.77
S <sub>6</sub> (Residue)			1.77
Total			29.56
Loss during distillation			0.29

Fractions S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>—By repeated fractional crystallisation from dilute acetone, palmitic acid melting point 62°C. was isolated from each of these fractions. This melting point was not depressed by the addition of an authentic sample of palmitic acid.

Fractions S<sub>4</sub> and S<sub>5</sub>—Palmitic acid M. P. 62°C. and stearic acid M. P. 68°C. were isolated from both S<sub>4</sub> and S<sub>5</sub> by repeated fractional crystallisations.

from dilute acetone. These melting points were not depressed by the addition of authentic samples of palmitic and stearic acids.

**Fraction  $S_8$  (Residue)**—The acids liberated from this fraction after saponification were dirty brown in colour. On extracting this mass with petroleum ether (40–60°C) an acid was obtained which after crystallisation from dilute acetone melted at 68°C (not depressed by the addition of pure stearic acid). The molecular weight was found to be 282.2 (stearic acid = 284).

TABLE VIII

Fract No	Iodine value	Sap value	Sap equiv	Palmitic %	Acid gms.	Stearic %	gms	Unsaturated %	acids gms
$S_1$	0.7	207.4	270.6	92.92	5.667	1.37	0.083	0.54	0.033
$S_2$	1.1	204.1	274.9	77.52	7.628	16.54	1.628	0.84	0.083
$S_3$	2.1	203.5	275.7	74.69	2.839	18.75	0.713	1.60	0.061
$S_4$	3.1	199.5	281.1	57.71	3.047	34.82	1.839	2.37	0.125
$S_5$	4.3	196.3	285.8	40.85	1.132	50.93	1.411	3.29	0.091
$S_6$	4.7	186.1	301.5			96.41	0.961	3.59	0.036
Total					20.313		6.635		0.429

Residue—polymerised 0.733 gms

unpolymerised 0.997 gms

Hence composition of solid acids is—palmitic 75.38% and stearic 24.62% and in mixed acids palmitic acid 3.67% and stearic acid 1.20%

The fatty acids of the oil of the seeds of *Pinus gerardiana* therefore consist of oleic, linoleic, palmitic and stearic acids, the percentages of which are given in table 9.

TABLE IX

	%
Oleic acid	52.33
Linoleic acid	42.80
Palmitic acid	3.67
Stearic acid	1.20

#### *Examination of the unsaponifiable matter*

The unsaponifiable matter obtained by extracting the soap solution with ether was a semi-solid mass having a light yellow colour. This was crystallised from alcohol whereby a compound melting at 133°C was obtained. This gave all the colour reactions of a phytosterol. It also gave

an acetyl derivative M. P.  $123^{\circ}\text{C}$ . Hence it was a phytosterol, sitosterol, found in most vegetable oils

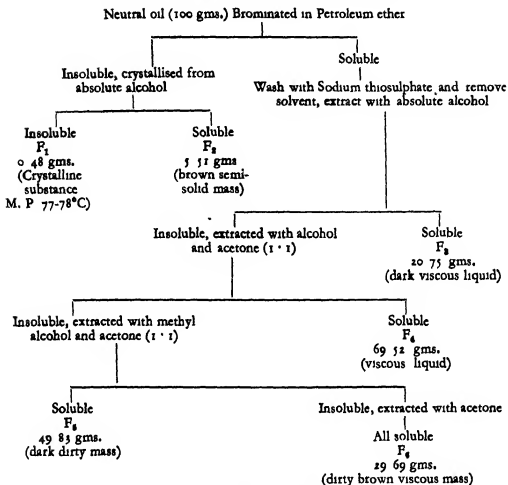
### *The Component Glycerides*

The oil was made neutral by treating it with sodium carbonate and purified with animal charcoal and Fuller's earth

Fifty grams of the neutral oil were then dissolved in six times its weight of dry acetone and kept in a frigidaire at  $0^{\circ}\text{C}$  for about a week. Nothing separated showing that the oil does not contain any fully saturated or disaturated glycerides.

Another lot of fifty gms of the neutral oil was dissolved in ten times its weight of dry acetone and oxidised with four times its weight of powdered potassium permanganate according to the method of Hilditch and Lea<sup>17</sup>. The process was repeated two times when in the end no neutral substance was left. This further confirms the absence of fully saturated glycerides.

One hundred grams of the neutral oil were then dissolved in ten times its weight of dry petroleum ether (B. P.  $40-60^{\circ}\text{C}$ ), cooled to  $-5^{\circ}\text{C}$  and bromine added till it was in slight excess which was indicated by the colour of the solution turning to permanently brown. This was kept overnight in a frigidaire when some semi-solid mass precipitated. This was filtered off and washed with chilled petroleum ether. The product left on the filter paper was crystallised from absolute alcohol when two fractions  $F_1$  and  $F_2$ , one alcohol insoluble and the other soluble were obtained. The petroleum ether filtrate and washings were mixed and treated with a solution of sodium thiosulphate to remove excess of bromine, washed with water, dehydrated and the solvent distilled off, when a dark viscous liquid was obtained. This was extracted with absolute alcohol and the alcohol-soluble portion was designated as  $F_3$ . The alcohol-insoluble portion was extracted with a mixture of absolute alcohol and acetone (1 : 1) and the soluble portion gave  $F_4$ . The insoluble portion was then extracted with methyl alcohol and acetone (1 : 1) and from the soluble portion  $F_5$  was obtained. The insoluble portion was completely soluble in acetone which gave  $F_6$ . The scheme of separation is shown below:—



The fractions  $F_1$ ,  $F_2$ ,  $F_4$ ,  $F_5$ , and  $F_6$  were debrominated. The debrominated products were saponified, the unsaponifiable matter removed with ether and the fatty acids liberated. The saponification equivalent, the iodine value and the thiocyanogen value of the liberated acids were then determined and from these the quantities of individual acids in each fraction were calculated. The amounts of saturated acids being too small they were considered as one acid. The acids were then oxidised with an alkaline solution of potassium permanganate according to the method of Lapworth and Mottram (*loc. cit.*), the unoxidised portion extracted with petroleum ether when it was found that only  $F_2$ ,  $F_3$ , and  $F_5$  gave saturated acids. This is also evident as a result of calculation from the thiocyanogen value. The saponification equivalent of saturated acids so obtained were determined.

As  $F_1$  was too small in amount to be subjected to the above operations, it was crystallised from absolute alcohol when a product M P  $77-78^\circ\text{C}$  was obtained. Its bromine content was determined by Piria and Schiff's method. The compound was found to be an impure sample of a triglyceride of tetrabromolinoleic acid. Found  $\text{Br}=51.31\%$ ,  $\text{C}_{57}\text{H}_{98}\text{O}_6$ ,  $\text{Br}_{18}$  requires  $\text{Br}=52.26\%$ . The melting point is, however, lower than that observed by the authors previously<sup>18</sup> but agrees with that observed by Vidyarthi and Mallya<sup>6</sup>.

The results of bromination and analysis are given in tables 10, 11, and 12.

The results obtained above are in fair agreement with those obtained for the component fatty acids of the oil which are also given (Mol. per cent) in table 12 in brackets for comparison.

TABLE X

	$F_1$	$F_2$	$F_3$	$F_4$	$F_5$	$F_6$
Wt of brominated product in gms	0.48	3.51	20.78	69.52	49.83	29.69
Wt of debrominated products in gms. (glyceride+unsaponifiable matter)	0.23	3.16	11.67	37.63	29.96	17.37
Wt of unsaponifiable matter		0.02	0.06	0.19	0.15	0.10
Wt of glycerides (free of unsaponifiable matter)	0.23	3.16	11.67	37.63	29.95	17.36
Mol % of mixed acids	0.23	3.19	11.73	37.57	29.98	17.30
Sap equiv of liberated acids		276.6	279.2	280.9	280.2	281.4
Iodine value (Hanus) of liberated acids		123.1	129.5	140.6	109.9	117.7
Thiocyanogen value (24 hours)		61.7	79.7	90.4	81.8	90.1
Sap equivalent of saturated acids		260.5	272.3		265.1	

TABLE XI

Mol. percentage of acids in each fraction

	$F_1$	$F_2$	$F_3$	$F_4$	$F_5$	$F_6$
Linoleic	0.23	3.19	11.73	37.57	29.98	17.30
Oleic	100	67.14	54.79	55.69	31.14	30.60
Saturated	..	..	32.92	44.31	59.12	69.40
		32.86	12.29		9.74	

TABLE XII

*Mol percentage of acids on total acids*

	F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	Total
Linoleic	0 23	2 14	6 43	20 93	9 32	5 30	44 33 (42 89)
Oleic			3 86	16 64	17 74	12 00	50 24 (52 04)
Saturated		1 05	1 44		2 92		5 41 (5 07)

TABLE XIII

*Probable component glycerides (Mol per cent)*

Glycerides in	F <sub>1</sub> 0 23	F <sub>2</sub> 3 19	F <sub>3</sub> 11 73	F <sub>4</sub> 37 57	F <sub>5</sub> 29 98	F <sub>6</sub> 17 30	Total 100 00
1 Fully saturated glycerides	nil	nil	nil	nil	nil	nil	
2 Disaturated glycerides	nil	nil	nil	nil	nil	nil	
3 Monosaturated glycerides							
(a) Saturated dilinolein		3 19					3 19
(b) Saturated oleolinolein			4 32		8 76		13 08
4 Triunsaturated glycerides							
(a) Trilinolein	0 23		0 15				0 38
(b) Oleodilinolein			7 26	25 22			32 48
(c) Dioleolinolein				12 35	19 20	15 90	47 45
(d) Triolein					2 02	1 40	3 42

From the above figures the probable component glycerides of the oil of the seeds of *Pinus gerardiana* have been calculated as shown in table 13.

In these calculations all the saturated acids have been considered as one acid. Also as all the saturated acids are combined as monosaturated diunsaturated glycerides, it can be assumed that they are proportionally distributed in monosaturated dilinolein and monosaturated oleolinolein. From these considerations the component glycerides of the oil of *Pinus gerardiana* seeds may be given as follows:—Palmitodilinolein 2.41%, stearodilinolein 0.78%, palmitooleolinolein 9.86%, stearooleolinolein 3.22%, trilinolein 0.38%, oleodilinolein 32.48%, dioleolinolein 47.45% and triolein 3.42%.



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# PROCEEDINGS

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### (SECTION A)

Part 3]

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### MOTION IN INCOMPRESSIBLE FLUID OF VARIABLE DENSITY II

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This paper is in continuation with other papers already published by the author in the Proceedings of the National Academy of Sciences. Here two cases of density variation have been considered, the laws of density being (i)  $\rho = \rho_0 + \lambda x$  and (ii)  $\rho = \rho_0/(1 + \lambda x)$ , where  $\rho_0$  is the value of  $\rho$  at the origin and  $\lambda$  is a constant, which is not necessarily small. We shall suppose that  $\rho$  is a constant for negative values of  $x$  and the coefficient of viscosity a constant throughout the motion. We shall further assume that  $u, v$  and  $w$  are small and small quantities of the second order will be neglected.

In the absence of extraneous forces, our equations of motion, in the case of an incompressible fluid, are

$$\rho \frac{Du}{Dt} = -\frac{\partial p}{\partial x} + \mu \nabla^2 u$$

$$\rho \frac{Dv}{Dt} = -\frac{\partial p}{\partial y} + \mu \nabla^2 v$$

$$\rho \frac{Dw}{Dt} = -\frac{\partial p}{\partial z} + \mu \nabla^2 w$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

If we neglect small quantities of the second order, the equations of motion reduce to,—

$$\rho \frac{\partial u}{\partial t} = -\frac{\partial p}{\partial x} + \mu \nabla^2 u$$

$$\rho \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial y} + \mu \nabla^2 v$$

$$\rho \frac{\partial w}{\partial t} = -\frac{\partial p}{\partial z} + \mu \nabla^2 w$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0.$$

Case I

$$\rho = \rho_0 + \lambda x$$

The equations of motion accordingly become

$$(\rho_0 + \lambda x) \frac{\partial u}{\partial t} = -\frac{\partial p}{\partial x} + \mu \nabla^2 u,$$

$$(\rho_0 + \lambda x) \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial y} + \mu \nabla^2 v,$$

$$(\rho_0 + \lambda x) \frac{\partial w}{\partial t} = -\frac{\partial p}{\partial z} + \mu \nabla^2 w,$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

If  $u$ ,  $v$  and  $w$  all vary as  $e^{\alpha_0 t}$ , where  $\alpha_0$  is a constant, the equations of motion take the form,

$$(\rho_0 + \lambda x) \alpha_0 u = -\frac{\partial p}{\partial x} + \mu \nabla^2 u, \quad . \quad . \quad . \quad . \quad (1)$$

$$(\rho_0 + \lambda x) \alpha_0 v = -\frac{\partial p}{\partial y} + \mu \nabla^2 v, \quad . \quad . \quad . \quad . \quad (2)$$

$$(\rho_0 + \lambda x) \alpha_0 w = -\frac{\partial p}{\partial z} + \mu \nabla^2 w, \quad . \quad . \quad . \quad . \quad (3)$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad . \quad . \quad . \quad . \quad (4)$$

Differentiating both sides of (1), (2) and (3) with respect to  $x$ ,  $y$  and  $z$  respectively and using (4), we get

$$\lambda \alpha_0 u = -\nabla^2 p. \quad . \quad . \quad . \quad . \quad (5)$$

Now we multiply both sides of (1) by  $\lambda \alpha_0$  and get

$$\alpha_0 (\rho_0 + \lambda x) \lambda \alpha_0 u = -\lambda \alpha_0 \frac{\partial p}{\partial x} + \mu \lambda \alpha_0 \nabla^2 u$$

$$\text{or } -\alpha_0 (\rho_0 + \lambda x) \nabla^2 p = -\lambda \alpha_0 \frac{\partial p}{\partial x} - \mu \nabla^2 (\nabla^2 p), \text{ by (5)}$$

$$\text{or } \mu \nabla^2 (\nabla^2 p) - \alpha_0 (\rho_0 + \lambda x) \nabla^2 p + \lambda \alpha_0 \frac{\partial p}{\partial x} = 0$$

$$\text{We put } \rho_0 + \lambda x = \lambda x_1, \text{ so that } \delta x = \delta x_1. \quad (6)$$

$$\text{Thus we get } \nabla^2 (\nabla^2 p) - \beta x_1 \nabla^2 p + \beta \frac{\partial p}{\partial x_1} = 0. \quad (7)$$

$$\text{where } \beta = \frac{\lambda \alpha_0}{\mu}, \text{ and } \nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Now (7) is the equation which will determine the pressure in this case.

Let us first solve (7).

Put  $p = p_1 p_2$ , where  $p_2$  is a function of  $y$  and  $z$  only, and  $p_1$  that of  $x$  or  $x_1$  only.

Thus

$$\nabla^2 \left( p_2 \frac{d^2 p_1}{dx_1^2} + p_1 \nabla_1^2 p_2 \right) - \beta x_1 \left( p_2 \frac{d^2 p_1}{dx_1^2} + p_1 \Delta_1^2 p_2 \right) + \beta p_2 \frac{dp_1}{dx_1} = 0$$

$$\text{or } p_2 \frac{d^4 p_1}{dx_1^4} + \frac{d^2 p_1}{dx_1^2} \nabla_1^2 p_2 + \frac{d^2 p_1}{dx_1^2} \nabla_1^2 p_2 + p_1 \nabla_1^2 (\nabla_1^2 p_2) - \beta x_1 \left( \frac{d^2 p_1}{dx_1^2} p_2 + p_1 \nabla_1^2 p_2 \right) + \beta p_2 \frac{dp_1}{dx_1} = 0$$

$$\text{or } p_2 \frac{d^4 p_1}{dx_1^4} + 2 \frac{d^2 p_1}{dx_1^2} \nabla_1^2 p_2 + p_1 \nabla_1^2 (\nabla_1^2 p_2) - \beta x_1 \left( \frac{d^2 p_1}{dx_1^2} p_2 + p_1 \nabla_1^2 p_2 \right) + \beta p_2 \frac{dp_1}{dx_1} = 0$$

This equation can be satisfied if we write

$$\nabla_1^2 p_2 + k p_2 = 0, \quad (8)$$

$$\text{and } p_2 \frac{d^4 p_1}{dx_1^4} - 2k p_2 \frac{d^2 p_1}{dx_1^2} + k^2 p_1 p_2 - \beta x_1 \left( p_2 \frac{d^2 p_1}{dx_1^2} - k p_2 p_2 \right) + \beta p_2 \frac{dp_1}{dx_1} = 0$$

$$\text{or } \frac{d^4 p_1}{dx_1^4} - 2k \frac{d^2 p_1}{dx_1^2} + k^2 p_1 - \beta x_1 \frac{d^2 p_1}{dx_1^2} + k \beta x_1 p_1 + \beta \frac{dp_1}{dx_1} = 0$$

$$\text{or } \frac{d^4 p_1}{dx_1^4} - (\beta x_1 + 2k) \frac{d^2 p_1}{dx_1^2} + \beta \frac{dp_1}{dx_1} + k (\beta x_1 + k) p_1 = 0 \quad (9)$$

Let  $D$  stand for the operator

$$\frac{d^4}{dx_1^4} - (\beta x_1 + 2k) \frac{d^3}{dx_1^3} + \beta \frac{d^2}{dx_1^2} + k(\beta x_1 + k)$$

so that

$$Dp_1 = 0.$$

For the solution of (9), we construct an expression

$$V \equiv \sum_{n=0}^{\infty} c_n x_1^{a+n} = c_0 x_1^a + c_1 x_1^{a+1} + c_2 x_1^{a+2} + \dots + c_n x_1^{a+n} + \dots$$

$$\begin{aligned} \text{so that } DV &= \sum c_0 [\alpha(\alpha-1)(\alpha-2)(\alpha-3)x_1^{a-4} - \beta\alpha(\alpha-1)x_1^{a-1} \\ &\quad - 2k\alpha(\alpha-1)x_1^{a-2} + \beta\alpha x_1^{a-1} + k\beta x_1^{a+1} + k^2 x_1^a] \\ &= c_0 [\alpha(\alpha-1)(\alpha-2)(\alpha-3)x_1^{a-4} - 2k\alpha(\alpha-1)x_1^{a-2} - \beta\alpha(\alpha-2)x_1^{a-1} \\ &\quad + k^2 x_1^a + k\beta x_1^{a+1}] \\ &+ c_1 [(\alpha+1)\alpha(\alpha-1)(\alpha-2)x_1^{a-3} - 2k(\alpha+1)\alpha x_1^{a-1} \\ &\quad - \beta(\alpha+1)(\alpha-1)x_1^a + k^2 x_1^{a+1} + k\beta x_1^{a+2}] \\ &+ c_2 [(\alpha+2)(\alpha+1)\alpha(\alpha-1)x_1^{a-2} - 2k(\alpha+2)(\alpha+1)x_1^a \\ &\quad - \beta(\alpha+2)\alpha x_1^{a+1} + k^2 x_1^{a+2} + k\beta x_1^{a+3}] \\ &+ c_3 [(\alpha+3)(\alpha+2)(\alpha+1)\alpha x_1^{a-1} - 2k(\alpha+3)(\alpha+2)x_1^{a+1} \\ &\quad - \beta(\alpha+3)(\alpha+2)x_1^{a+2} + k^2 x_1^{a+3} + k\beta x_1^{a+4}] \\ &+ c_4 [(\alpha+4)(\alpha+3)(\alpha+2)(\alpha+1)x_1^a - 2k(\alpha+4)(\alpha+3)x_1^{a+2} \\ &\quad - \beta(\alpha+4)(\alpha+2)x_1^{a+3} + k^2 x_1^{a+4} + k\beta x_1^{a+5}] \\ &+ c_5 [(\alpha+5)(\alpha+4)(\alpha+3)(\alpha+2)x_1^{a+1} - 2k(\alpha+5)(\alpha+4)x_1^{a+3} \\ &\quad - \beta(\alpha+5)(\alpha+3)x_1^{a+4} + k^2 x_1^{a+5} + k\beta x_1^{a+6}] \\ &+ \dots + c_{n-4} [(\alpha+n-4)(\alpha+n-5)(\alpha+n-6)(\alpha+n-7)x_1^{a+n-8} \\ &\quad - 2k(\alpha+n-4)(\alpha+n-5)x_1^{a+n-6} - \beta(\alpha+n-4)(\alpha+n-6)x_1^{a+n-5} \\ &\quad + k^2 x_1^{a+n-4} + k\beta x_1^{a+n-3}] \\ &+ c_{n-3} [(\alpha+n-3)(\alpha+n-4)(\alpha+n-5)(\alpha+n-6)x_1^{a+n-7} \\ &\quad - 2k(\alpha+n-3)(\alpha+n-4)x_1^{a+n-5} - \beta(\alpha+n-3)(\alpha+n-5)x_1^{a+n-4} \\ &\quad + k^2 x_1^{a+n-3} + k\beta x_1^{a+n-2}] \end{aligned}$$



$$\text{let } \frac{c_{n+1}}{c_n} = l + \varepsilon_1, \quad \frac{c_n}{c_{n-1}} = l + \varepsilon_2, \quad \frac{c_{n-1}}{c_{n-2}} = l + \varepsilon_3,$$

$$\frac{c_{n-2}}{c_{n-3}} = l + \varepsilon_4 \quad \text{and} \quad \frac{c_{n-3}}{c_{n-4}} = l + \varepsilon_5, \quad \text{where the } \varepsilon' s \rightarrow 0,$$

$$\text{as } n \rightarrow \infty.$$

$$\begin{aligned} \text{Thus } \frac{c_{n+1}}{c_{n-4}} &= \frac{c_{n+1}}{c_n} \cdot \frac{c_n}{c_{n-1}} \cdot \frac{c_{n-1}}{c_{n-2}} \cdot \frac{c_{n-2}}{c_{n-3}} \cdot \frac{c_{n-3}}{c_{n-4}} \\ &= (l + \varepsilon_1) (l + \varepsilon_2) (l + \varepsilon_3) (l + \varepsilon_4) (l + \varepsilon_5), \quad \text{etc.} \end{aligned}$$

Substituting the values we get

$$\begin{aligned} (l + \varepsilon_1) (l + \varepsilon_2) (l + \varepsilon_3) (l + \varepsilon_4) (l + \varepsilon_5) &= \frac{2L}{o_1 (n^3)} (l + \varepsilon_2) (l + \varepsilon_4) (l + \varepsilon_5) \\ &+ \frac{\beta}{o_2 (n^3)} (l + \varepsilon_4) (l + \varepsilon_5) - \frac{k^2}{o_1 (n^4)} (l + \varepsilon_5) - \frac{k\beta}{o_2 (n^4)} \end{aligned}$$

Taking limits as  $n \rightarrow \infty$ , we see that  $l \rightarrow o$ .

The series thus obtained will be absolutely and uniformly convergent for all values of  $x_1$ . Now our indicial equation is

$$\alpha (\alpha - 1) (\alpha - 2) (\alpha - 3) = 0,$$

so that the roots are 3, 2, 1 and zero.

Thus the four solutions will be given by, <sup>(1)</sup>

$$p_1' = \left[ V \right]_{\alpha=3}, \quad p_1'' = \left[ \frac{\partial V}{\partial \alpha} \right]_{\alpha=2}, \quad p_1''' = \left[ \frac{\partial^2 V}{\partial \alpha^2} \right]_{\alpha=1} \quad \text{and} \quad p_1'''' = \left[ \frac{\partial^3 V}{\partial \alpha^3} \right]_{\alpha=0} \quad (17)$$

As regards (8), we have <sup>(2)</sup>

$$\left. \begin{aligned} p_1 &= A_m J_m (\beta_1 \omega) \frac{\cos}{\sin} \left\{ m\phi, \text{ if } k = \beta_1 \right\} \\ \text{or} \quad B_1 I_0 (\beta_2 \omega) \frac{\cos}{\sin} \left\{ s\phi, \text{ if } k = -\beta_1 \right\} \end{aligned} \right\} \quad (18)$$

where  $\omega = \sqrt{y^2 + z^2}$  and  $\tan \phi = \frac{z}{y}$

Thus  $p$  is determined.

Now we have to find  $u$ ,  $v$  and  $w$ . Substituting  $p_0 + \lambda x = \lambda x_1$  in (1), (2), (8) and (4), we have

$$\lambda \alpha_0 x_1 u = - \frac{\partial p}{\partial x_1} + \mu \nabla^2 u, \quad \dots \quad (11)$$

$$\lambda \alpha_0 x_1 v = - \frac{\partial p}{\partial y} + \mu \nabla^2 v, \quad \dots \quad (21)$$

$$\lambda \alpha_0 x_1 w = -\frac{\partial p}{\partial x} + \mu \nabla^2 v, \quad . \quad . \quad . \quad . \quad . \quad (31)$$

$$\text{with} \quad \frac{\partial u}{\partial x_1} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

Again from (5)

$$\text{Let } \left\{ \begin{array}{l} \lambda \alpha_0 u = -\nabla^2 p = -p_1 \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right), \\ \lambda \alpha_0 v = -\frac{\partial p_1}{\partial y} v_0 \\ \text{and } \lambda \alpha_0 w = -\frac{\partial p_1}{\partial x} w_0 \end{array} \right\} \quad (19)$$

where  $v_0$  and  $w_0$  are functions of  $x_1$  only

It is quite evident that  $v_0 = w_0$ .

$$\text{Now} \quad \lambda \alpha_0 x_1 v = -\frac{\partial p}{\partial y} + \mu \nabla^2 v.$$

$$\text{or } -x_1 \frac{\partial p_1}{\partial y} v_0 = -\frac{\partial p_1}{\partial y} p_1 - \frac{\mu}{\lambda \alpha} \nabla^2 \left( \frac{\partial p_1}{\partial y} v_0 \right)$$

$$\text{or } -x_1 \frac{\partial p_1}{\partial y} v_0 = -\frac{\partial p_1}{\partial y} p_1 - \frac{\mu}{\lambda \alpha} \left( \frac{d^2 v_0}{dx_1^2} \frac{\partial p_1}{\partial y} - k v_0 \frac{\partial p_1}{\partial y} \right)$$

$$\text{or} \quad \beta x_1 v_0 = \beta p_1 + \frac{d^2 v_0}{dx_1^2} - k v_0$$

Hence  $v_0$  is given by

$$\frac{d^2 v_0}{dx_1^2} - (\beta x_1 + k) v_0 = -\beta p_1, \quad . \quad . \quad . \quad . \quad (20)$$

Now we have to find the solution of

$$\lambda \alpha_0 x_1 u_1 = \mu \nabla^2 u_1$$

$$\lambda \alpha_0 x_1 v_1 = \mu \nabla^2 v_1$$

$$\lambda \alpha_0 x_1 w_1 = \mu \nabla^2 w_1$$

with

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0$$

i.e.,

$$(\nabla^2 - k_0 x_1) u_1 = 0$$

$$(\nabla^2 - k_0 x_1) v_1 = 0$$

$$(\nabla^2 - k_0 x_1) w_1 = 0$$

with

$$\frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0, \text{ where } k_0 = \frac{\lambda \alpha_0}{\mu}$$





Hence a complete solution is given by

$$e^{-\alpha_0 t} u = -\frac{p_2}{\lambda \alpha_0} \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right)$$

$$e^{-\alpha_0 t} v = R \frac{\partial S}{\partial x} - \frac{1}{\lambda \alpha_0} \frac{\partial p_2}{\partial y} v_0$$

$$e^{-\alpha_0 t} w = -R \frac{\partial S}{\partial y} - \frac{1}{\lambda \alpha_0} \frac{\partial p_2}{\partial x} v_0$$

Differentiating both sides of the first, second and third of (19) with  $x_1$ ,  $y$  and  $z$  respectively and adding and then using (4.1), we find that  $v_0$  should be given by

$$\frac{d}{dx_1} \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right) = k v_0$$

or 
$$k v_0 = \frac{d^3 p_1}{dx_1^3} - k \frac{d p_1}{dx_1}, \quad . \quad . \quad . \quad (21)$$

So in order that our supposition may be justified, we have to show that the  $v_0$ 's, given by (20) and (21) are the same

From (21), 
$$k v_0 = \frac{d^3 p_1}{dx_1^3} - k \frac{d p_1}{dx_1}$$

or 
$$k \frac{d v_0}{dx_1} = \frac{d^4 p_1}{dx_1^4} - k \frac{d^2 p_1}{dx_1^2}$$

$$= (\beta x_1 + l) \frac{d^2 p_1}{dx_1^2} - \beta \frac{d p_1}{dx_1} - l (\beta x_1 + l) p_1, \text{ from (9)}$$

Again 
$$k \frac{d^2 v_0}{dx_1^2} = (\beta x_1 + l) \frac{d^3 p_1}{dx_1^3} - l (\beta x_1 + l) \frac{d p_1}{dx_1} - l \beta p_1$$

or 
$$\left[ \frac{d^2 v_0}{dx_1^2} - (\beta x_1 + l) v_0 \right] = -\beta p_1, \text{ which is the same as (20)}$$

Hence, the justification.

Thus 
$$u = -\frac{e^{\alpha_0 t}}{\lambda \alpha_0} p_2 \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right)$$

$$v = \frac{e^{\alpha_0 t}}{\lambda \alpha_0} \frac{\partial p_2}{\partial y} v_0$$

$$w = -\frac{e^{\alpha_0 t}}{\lambda \alpha_0} \frac{\partial p_2}{\partial x} v_0, \text{ where } v_0 \text{ is given by (21).}$$

The case, when the left-hand sides of our original equations of motion vanish, has been already solved.<sup>(1)</sup> Thus a complete solution is given by

$$u = -\frac{e^{a_0 t}}{\lambda \alpha_0} p_1 \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right) + \frac{1}{\mu} \sum \left\{ \frac{r^2}{2(2n+1)} \frac{dp_n}{dx} \right. \\ \left. + \frac{n r^{2n+2}}{(n+1)(2n+1)(2n+3)} \frac{\partial}{\partial x} \frac{p_n}{r^{2n+1}} \right\} + u', \\ v = -\frac{e^{a_0 t}}{\lambda \alpha_0} \frac{\partial p_2}{\partial y} r_0 + \frac{1}{\mu} \sum \left\{ \frac{r^2}{2(2n+1)} \frac{\partial p_n}{\partial y} + \frac{n r^{2n+2}}{(n+1)(2n+1)(2n+3)} \frac{\partial}{\partial y} \right. \\ \left. \frac{p_n}{r^{2n+1}} \right\} + v',$$

and

$$w = -\frac{e^{a_0 t}}{\lambda \alpha_0} \frac{\partial p_3}{\partial z} r_0 + \frac{1}{\mu} \sum \left\{ \frac{r^2}{2(2n+1)} \frac{\partial p_n}{\partial z} + \frac{n r^{2n+2}}{(n+1)(2n+1)(2n+3)} \frac{\partial}{\partial z} \right. \\ \left. \frac{p_n}{r^{2n+1}} \right\} + w'.$$

Case II.

$$\rho = \rho_0 / (1 + \lambda x).$$

The equations of motion become

$$\rho_0 \frac{\partial u}{\partial t} = -(1 + \lambda x) \frac{\partial p}{\partial x} + \mu(1 + \lambda x) \nabla^2 u$$

$$\rho_0 \frac{\partial v}{\partial t} = -(1 + \lambda x) \frac{\partial p}{\partial y} + \mu(1 + \lambda x) \nabla^2 v$$

$$\rho_0 \frac{\partial w}{\partial t} = -(1 + \lambda x) \frac{\partial p}{\partial z} + \mu(1 + \lambda x) \nabla^2 w$$

with

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

Put  $1 + \lambda x = \lambda x_1$ , so that  $\delta x = \delta x_1$ .

and let  $u, v$  and  $w$ , all vary as  $\exp \alpha t$ , so that our equations of motion are modified to

$$\left. \begin{aligned} \bar{\alpha} u &= -\lambda_0 x_1 \frac{\partial p}{\partial x_1} + \lambda_0 \mu x_1 \nabla^2 u \\ \bar{\alpha} v &= -\lambda_0 x_1 \frac{\partial p}{\partial y} + \lambda_0 \mu x_1 \nabla^2 v \\ \bar{\alpha} w &= -\lambda_0 x_1 \frac{\partial p}{\partial z} + \lambda_0 \mu x_1 \nabla^2 w \end{aligned} \right\} \quad . \quad . \quad . \quad (1)$$

with 
$$\frac{\partial u}{\partial x_1} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad (2)$$

where 
$$\nabla^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \text{ and } \lambda_0 = \frac{\lambda}{\rho_0}$$

From (1) we get

$$\mu \left( \frac{\partial u}{\partial x_1} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) = -\lambda_0 x_1 \nabla^2 p - \lambda_0 \frac{\partial p}{\partial x_1} + \lambda_0 \mu r_1 \nabla^2 \left( \frac{\partial u}{\partial x_1} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) + \lambda_0 \mu \nabla^2 u$$

or 
$$0 = -\lambda_0 x_1 \nabla^2 p - \lambda_0 \frac{\partial p}{\partial x_1} + \lambda_0 \mu \nabla^2 u, \quad \text{by (2)}$$

or 
$$\mu \nabla^2 u = x_1 \nabla^2 p + \frac{\partial p}{\partial x_1} \quad (3)$$

From the first equation of (1)

$$\alpha u = \lambda_0 x_1 \left( \mu \nabla^2 u - \frac{\partial p}{\partial x_1} \right) = \lambda_0 x_1^2 \nabla^2 p, \quad (4)$$

Now we substitute the value of  $u$  from (4) to (3), so that

$$\mu \lambda_0 \nabla^2 (x_1^2 \nabla^2 p) = \alpha \left( x_1 \nabla^2 p + \frac{\partial p}{\partial x_1} \right)$$

or 
$$\nabla^2 (x_1^2 \nabla^2 p) - \alpha_0 \left( x_1 \nabla^2 p + \frac{\partial p}{\partial x_1} \right) = 0, \quad \text{where } \alpha_0 = \frac{\alpha}{\mu \lambda_0}$$

or 
$$x_1^2 \nabla^2 (\nabla^2 p) + 4x_1 \frac{\partial}{\partial x_1} \nabla^2 p + (2 - \alpha_0 x_1) \nabla^2 p - \alpha_0 \frac{\partial p}{\partial x_1} = 0$$

This equation will determine " $p$ ".

Put  $p = p_1 p_2$ , where  $p_1$  is a function of  $x_1$  alone and  $p_2$  that of  $y$  and  $z$  only, so that

$$x_1^2 \left\{ p_2 \frac{d^4 p_1}{dx_1^4} + 2 \frac{d^2 p_1}{dx_1^2} \nabla_1^2 p_2 + p_1 \nabla_1^2 (\nabla_1^2 p_2) \right\} + 4x_1 \frac{\partial}{\partial x_1} \left( \frac{d^2 p_1}{dx_1^2} p_2 + p_1 \nabla_1^2 p_2 \right) + (2 - \alpha_0 x_1) \left( \frac{d^2 p_1}{dx_1^2} p_2 + p_1 \nabla_1^2 p_2 \right) - \alpha_0 p_2 \frac{dp_1}{dx_1} = 0, \text{ where } \nabla_1^2 = \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Now this equation can be satisfied if we write

$$\nabla_1^2 p_2 + k p_2 = 0, \quad (5)$$

and 
$$x_1^2 \left( \frac{d^4 p_1}{dx_1^4} - 2k \frac{d^2 p_1}{dx_1^2} + k^2 p_1 \right) + 4x_1 \left( \frac{d^2 p_1}{dx_1^2} - k \frac{dp_1}{dx_1} \right) + (2 - \alpha_0 x_1) \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right) - \alpha_0 \frac{dp_1}{dx_1} = 0$$

$$\text{or } x_1^2 \frac{d^4 p_1}{dx_1^4} + 4x_1 \frac{d^3 p_1}{dx_1^3} + (2 - \alpha_0 x_1 - 2kx_1^2) \frac{d^2 p_1}{dx_1^2} - (\alpha_0 + 4kx_1) \frac{dp_1}{dx_1} - k(2 - \alpha_0 x_1 - kx_1^2) p_1 = 0. \quad (6)$$

$$\text{Let } D = x_1^2 \frac{d^4}{dx_1^4} + 4x_1 \frac{d^3}{dx_1^3} + (2 - \alpha_0 x_1 - 2kx_1^2) \frac{d^2}{dx_1^2} - (\alpha_0 + 4kx_1) \frac{d}{dx_1} - k(2 - \alpha_0 x_1 - kx_1^2)$$

We construct an expression

$$V = \sum_{n=0}^{\infty} c_n x_1^{a+n}$$

so that

$$\begin{aligned} DV &= \sum c_0 [a(a-1)(a-2)(a-3)x_1^{a-2} + 4a(a-1)(a-2)x_1^{a-2} + (2 - \alpha_0 x_1 - 2kx_1^2) \\ &\quad a(a-1)x_1^{a-2} - (\alpha_0 + 4kx_1)a x_1^{a-1} - k(2 - \alpha_0 x_1 - kx_1^2)x_1^a] \\ &= \sum c_0 [a(a-1)\{(a-2)(a-3) + 4(a-2) + 2\}x_1^{a-2} - \alpha_0 a(a-1+1)x_1^{a-1} \\ &\quad + x_1^a \{-2ka(a-1) - 4ka - 2k\} + k\alpha_0 x_1^{a+1} + k^2 x_1^{a+2}] \\ &= c_0 [a^2(a-1)^2 x_1^{a-2} - \alpha_0^2 x_1^{a-1} - 2k\{a(a+1)+1\}x_1^a + k\alpha_0 x_1^{a+1} \\ &\quad + k^2 x_1^{a+2}] \\ &+ c_1 [(a+1)^2 a^2 x_1^{a-1} - (a+1)^2 \alpha_0 x_1^a - 2k\{(a+1)(a+2)+1\}x_1^{a+1} \\ &\quad + k\alpha_0 x_1^{a+2} + k^2 x_1^{a+3}] \\ &+ c_2 [(a+2)^2 (a+1)^2 x_1^a - (a+2)^2 \alpha_0 x_1^{a+1} - 2k\{(a+2)(a+3)+1\}x_1^{a+2} \\ &\quad + k\alpha_0 x_1^{a+3} + k^2 x_1^{a+4}] \\ &+ c_3 [(a+3)^2 (a+2)^2 x_1^{a+1} - (a+3)^2 \alpha_0 x_1^{a+2} - 2k\{(a+3)(a+4)+1\} \\ &\quad x_1^{a+3} + k\alpha_0 x_1^{a+4} + k^2 x_1^{a+5}] \\ &+ c_4 [(a+4)^2 (a+3)^2 x_1^{a+2} - (a+4)^2 \alpha_0 x_1^{a+3} - 2k\{(a+4)(a+5)+1\} \\ &\quad x_1^{a+4} + k\alpha_0 x_1^{a+5} + k^2 x_1^{a+6}] \\ &+ \dots + \dots + \dots + \dots + \dots \\ &+ \dots + \dots + \dots + \dots + \dots \end{aligned}$$



Thus the four solutions will be given by,<sup>(1)</sup>

$$p_1' = [V]_{a=1} \quad p_1'' = \left[ \frac{\partial V}{\partial a} \right]_{a=1}, \quad p_1''' = \left[ \frac{\partial^2 V}{\partial a^2} \right]_{a=0} \quad \text{and} \quad p_1'''' = \left[ \frac{\partial^3 V}{\partial a^3} \right]_{a=0}. \quad (7)$$

For the solution of (5), we look to the solution of (8) in Case (i)

$$\text{Now} \quad \bar{a}u = \lambda_0 x_1^2 \nabla^2 p = \lambda_0 p_1 x_1^2 \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right)$$

$$\text{Suppose} \quad \begin{cases} \bar{a}v = \lambda_0 \frac{\partial p_1}{\partial y} v_0 \\ \bar{a}w = \lambda_0 \frac{\partial p_1}{\partial x} w_0 \end{cases} \quad (8)$$

where  $v_0$  and  $w_0$  are functions of  $x_1$  only. Evidently  $v_0 = w_0$

Since

$$\frac{\partial u}{\partial x_1} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0$$

We have

$$\lambda_0 p_1 \left[ x_1^2 \left( \frac{d^2 p_1}{dx_1^2} - k \frac{dp_1}{dx_1} \right) + 2x_1 \left( \frac{d^2 p_1}{dx_1^2} - k p_1 \right) \right] - \lambda_0 k p_1 v_0 = 0$$

$$\text{so that} \quad \lambda v_0 = x_1^2 \frac{d^2 p_1}{dx_1^2} + 2x_1 \frac{d^2 p_1}{dx_1^2} - k x_1^2 \frac{dp_1}{dx_1} - 2k x_1 p_1 \quad (9)$$

Again

$$\bar{a}^2 v = -\bar{a} \lambda_0 x_1 \frac{\partial p_1}{\partial y} p_1 + \mu \lambda_0 x_1 \nabla^2 (\bar{a}v), \quad \text{from (1)}$$

$$\text{or} \quad \bar{a} \lambda_0 \frac{\partial p_1}{\partial y} v_0 = -\bar{a} \lambda_0 x_1 \frac{\partial p_1}{\partial y} p_1 + \lambda_0 \mu \lambda_0 x_1 \nabla^2 \left( v_0 \frac{\partial p_1}{\partial y} \right),$$

$$\text{or} \quad \bar{a} \frac{\partial p_1}{\partial y} v_0 = -\bar{a} x_1 \frac{\partial p_1}{\partial y} p_1 + \lambda_0 \mu x_1 \frac{\partial p_1}{\partial y} \left( \frac{d^2 v_0}{dx_1^2} - k v_0 \right)$$

$$\text{or} \quad x_1 \left( \frac{d^2 v_0}{dx_1^2} - k v_0 \right) - \alpha_0 x_1 p_1 = \alpha_0 v_0$$

$$\text{or} \quad x_1 \frac{d^2 v_0}{dx_1^2} - (\alpha_0 + k x_1) v_0 = \alpha_0 x_1 p_1 \quad (10)$$

Thus in order that our supposition may be valid we must show that the  $v_0$ 's given by (9) and (10) are not different.

Now, from (9),

$$kv_0 = x_1^2 \frac{d^3 p_1}{dx_1^3} + 2x_1 \frac{d^2 p_1}{dx_1^2} - \lambda x_1^2 \frac{dp_1}{dx_1} - 2\lambda x_1 p_1$$

$$\text{or } \lambda \frac{dv_0}{dx_1} = x_1^2 \frac{d^4 p_1}{dx_1^4} + 4x_1 \frac{d^3 p_1}{dx_1^3} + (2 - \lambda x_1^2) \frac{d^2 p_1}{dx_1^2} - 4\lambda x_1 \frac{dp_1}{dx_1} - 2\lambda p_1$$

$$= (\alpha_0 x_1 + l x_1^2) \frac{d^3 p_1}{dx_1^3} + \alpha_0 \frac{dp_1}{dx_1} - \lambda (\alpha_0 x_1 + l x_1^2) p_1, \text{ by (6)}$$

$$k \frac{d^2 v_0}{dx_1^2} = (\alpha_0 x_1 + \lambda x_1^2) \frac{d^4 p_1}{dx_1^4} + (2\alpha_0 + 2\lambda x_1) \frac{d^3 p_1}{dx_1^3} - \lambda (\alpha_0 x_1 + l x_1^2) \frac{dp_1}{dx_1} - l' \alpha_0 + 2\lambda x_1 p_1$$

$$\text{so that } \lambda x_1 \frac{d^2 v_0}{dx_1^2} = x_1^2 (\alpha_0 + \lambda x_1) \frac{d^4 p_1}{dx_1^4} + 2x_1 (\alpha_0 + \lambda x_1) \frac{d^3 p_1}{dx_1^3} - \lambda x_1^2 (\alpha_0 + l x_1) \frac{dp_1}{dx_1} - \lambda x_1 (\alpha_0 + 2\lambda x_1) p_1$$

$$\lambda (\alpha_0 + \lambda x_1) v_0 = x_1^2 (\alpha_0 + \lambda x_1) \frac{d^3 p_1}{dx_1^3} + 2x_1 (\alpha_0 + \lambda x_1) \frac{d^2 p_1}{dx_1^2} - \lambda x_1^2 (\alpha_0 + \lambda x_1) \frac{dp_1}{dx_1} - 2\lambda x_1 (\alpha_0 + \lambda x_1) p_1$$

$$\lambda \left[ x_1 \frac{d^2 v_0}{dx_1^2} - (\alpha_0 + \lambda x_1) v_0 \right] = \lambda x_1 \alpha_0 p_1$$

This is our (10).

Hence the validity.

Now we have to find the solution of

$$\left. \begin{aligned} \bar{\alpha} u_1 &= \lambda_0 \mu x_1 \nabla^2 u_1 \\ \bar{\alpha} v_1 &= \lambda_0 \mu x_1 \nabla^2 v_1 \\ \bar{\alpha} w_1 &= \lambda_0 \mu x_1 \nabla^2 w_1 \end{aligned} \right\}$$

$$\text{subject to } \frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0,$$

$$\text{i.e., } (x_1 \nabla^2 - \alpha_0) (u_1, v_1, w_1) = 0$$

$$\text{subject to } \frac{\partial u_1}{\partial x_1} + \frac{\partial v_1}{\partial y} + \frac{\partial w_1}{\partial z} = 0, \quad \text{where } \alpha_0 = \frac{\bar{\alpha}}{\lambda_0 \mu}.$$

But  $u_1$ ,  $v_1$  and  $w_1$  have been already found.<sup>(2)</sup>



Thus a complete solution is given by

$$e^{-\alpha/u} = u_1 + \frac{\lambda_0}{\alpha} p_1 x_1^2 \left( \frac{d^2 p_1}{dx_1^2} - 1/p_1 \right)$$

$$e^{-\alpha/v} = v_1 + \frac{\lambda_0}{\alpha} \frac{\partial p_1}{\partial y} \quad (10)$$

$$e^{-\alpha/w} = w_1 + \frac{\lambda_0}{\alpha} \frac{\partial p_1}{\partial x} \quad (11)$$

I am grateful to Prof. A. C. Banerji for his kind help and encouragement in bringing out this paper.

### References

- 1 Forsyth *Theory of Differential Equations* Part III Vol. IV 1902 § 38, p. 33
- 2 *Proc. Nat. Acc. Sci.* Vol. 12 part 2 page 127
- 3 *Proc. Nat. Acc. Sci.*, Vol. 12 Part 3 page 158.

# FLUID MOTIONS OF THE TYPE $\xi_1 = \lambda_1 u_1$ , ETC. AND $\xi_2 = \lambda_2 u_2$ , ETC.

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In a previous paper\* we have shown that two motions in which the vortex lines of one coincide with the stream lines of the other can be superimposed upon one another so that the resulting velocity is the sum of the two velocities. The present paper† aims at discussing such motions.

An extension of Bernoulli's theorem has been obtained for a class of these motions and they have been shown to exist by choosing a particular case of uniplanar motions.

1 If  $\xi_1, \eta_1, \zeta_1; u_1, v_1, w_1$  be the vorticity and velocity components of one motion and  $\xi_2, \eta_2, \zeta_2; u_2, v_2, w_2$  the corresponding quantities of the other, the fact that the vortex lines of either system coincide with the stream lines of the other is symbolically represented by

$$\begin{array}{lll} \xi_1 = \lambda_1 u_1 & & \xi_2 = \lambda_2 u_2 \\ \eta_1 = \lambda_1 v_1 & \text{and} & \eta_2 = \lambda_2 v_2 \\ \zeta_1 = \lambda_1 w_1 & & \zeta_2 = \lambda_2 w_2 \end{array} \quad \text{I}$$

where  $\lambda_1$  and  $\lambda_2$  are functions of  $x, y, z$  and  $t$

Now,

$$\begin{aligned} \lambda_1 u_2 = \xi_1 &= \frac{\partial w_1}{\partial y} - \frac{\partial v_1}{\partial x} = \frac{\partial}{\partial y} \left( \frac{\zeta_1}{\lambda_1} \right) - \frac{\partial}{\partial x} \left( \frac{\eta_1}{\lambda_1} \right) \\ &= \frac{\partial}{\partial y} \left\{ \frac{1}{\lambda_1} \left( \frac{\partial v_2}{\partial x} - \frac{\partial u_2}{\partial y} \right) \right\} - \frac{\partial}{\partial x} \left\{ \frac{1}{\lambda_1} \left( \frac{\partial u_2}{\partial x} - \frac{\partial w_2}{\partial y} \right) \right\} \\ &= \frac{1}{\lambda_1} \frac{\partial}{\partial y} \left( \frac{\partial v_2}{\partial x} - \frac{\partial u_2}{\partial y} \right) - \frac{1}{\lambda_1} \frac{\partial}{\partial x} \left( \frac{\partial u_2}{\partial x} - \frac{\partial w_2}{\partial y} \right) \\ &\quad + \frac{1}{\lambda_1} \left( \frac{\partial \lambda_1}{\partial x} v_1 - \frac{\partial \lambda_1}{\partial y} w_1 \right) \end{aligned}$$

\*Superposable Fluid Motions. *Proc. R. Soc. Math. Soc.*, Vol. II, New Series (1940), p. 74, equ. (42).

†My thanks are due to Professor J. A. Strang for his interest and suggestions in this investigation.

and using the continuity condition of  $(u_2, v_2, w_2)$ , we get

$$\left. \begin{aligned} (\nabla^2 + \lambda_1 \lambda_2) u_2 &= v_1 \frac{\partial \lambda_1}{\partial x} - w_1 \frac{\partial \lambda_1}{\partial y} \\ (\nabla^2 + \lambda_1 \lambda_2) v_2 &= w_1 \frac{\partial \lambda_1}{\partial x} - u_1 \frac{\partial \lambda_1}{\partial y} \\ (\nabla^2 + \lambda_1 \lambda_2) w_2 &= u_1 \frac{\partial \lambda_1}{\partial y} - v_1 \frac{\partial \lambda_1}{\partial x} \end{aligned} \right\} \quad \text{II}$$

and

$$\left. \begin{aligned} (\nabla^2 + \lambda_1 \lambda_2) u_1 &= v_2 \frac{\partial \lambda_2}{\partial x} - w_2 \frac{\partial \lambda_2}{\partial y} \\ (\nabla^2 + \lambda_1 \lambda_2) v_1 &= w_2 \frac{\partial \lambda_2}{\partial x} - u_2 \frac{\partial \lambda_2}{\partial y} \\ (\nabla^2 + \lambda_1 \lambda_2) w_1 &= u_2 \frac{\partial \lambda_2}{\partial y} - v_2 \frac{\partial \lambda_2}{\partial x} \end{aligned} \right\} \quad \text{III}$$

To these we add

$$u_1 \frac{\partial \lambda_1}{\partial x} + v_1 \frac{\partial \lambda_1}{\partial y} + w_1 \frac{\partial \lambda_1}{\partial z} = 0 \quad \text{(i)}$$

and

$$u_2 \frac{\partial \lambda_2}{\partial x} + v_2 \frac{\partial \lambda_2}{\partial y} + w_2 \frac{\partial \lambda_2}{\partial z} = 0 \quad \text{(ii)}$$

deduced from I with the help of the continuity conditions of the two motions.

(i) states that the surfaces  $\lambda_1 = \text{constant}$  contain the stream lines of the motion  $(u_1, v_1, w_1)$  and consequently the vortex lines of the motion  $(u_2, v_2, w_2)$  and (ii) states that the surfaces  $\lambda_2 = \text{constant}$  contain the stream lines of the motion  $(u_2, v_2, w_2)$  and the vortex lines of the motion  $(u_1, v_1, w_1)$ .

If  $\lambda_1 = \lambda_2 = \lambda$ , the stream lines of the motion  $u_1 + u_2, v_1 + v_2, w_1 + w_2$ , obtained as a result of superposition coincide with its vortex lines and  $\lambda$  has the properties deduced in two previous papers\*. One of the types of resulting motion in this particular case decays exponentially with time and satisfies Bernoulli's theorem.

2 If the two motions are uniplanar, we may by taking the planes of motion parallel to  $z = \text{constant}$  have  $w_1 = w_2 = 0$ . The last equations of II and III then give

$$\begin{aligned} u_1 \frac{\partial \lambda_1}{\partial y} - v_1 \frac{\partial \lambda_1}{\partial x} &= 0 \\ u_2 \frac{\partial \lambda_2}{\partial y} - v_2 \frac{\partial \lambda_2}{\partial x} &= 0 \end{aligned}$$

\*Self-superposable Motions of the type  $\xi = \lambda u$  etc., . . . *Proc. Benares Math. Soc.*, Vol. II, New Series (1940), pp. 86-89.

On Superposability . . . *Jour. Indian Math. Soc.*, Vol. VI, March (1942), pp. 33-40.

and equations (i) and (ii) reduce to

$$u_1 \frac{\partial \lambda_1}{\partial x} + v_1 \frac{\partial \lambda_1}{\partial y} = 0$$

$$u_2 \frac{\partial \lambda_2}{\partial x} + v_2 \frac{\partial \lambda_2}{\partial y} = 0$$

from which it follows that both  $\lambda_1$  and  $\lambda_2$  are independent of  $x$  and  $y$

That is, for uniplanar motions the proportionality factor between the vorticity of one motion and the velocity of the other depends only on time and the distance of the plane of motion from some fixed parallel plane

3 If  $\lambda_1$  and  $\lambda_2$  are independent of  $x, y, z$ , equations II and III reduce to

$$(\nabla^2 + \lambda_1 \lambda_2) (u_1, v_1, w_1) = 0 \quad \text{IV}$$

$$(\nabla^2 + \lambda_1 \lambda_2) (u_2, v_2, w_2) = 0 \quad \text{V}$$

from which we see that if any one of the velocity components of one of the motions is harmonic and non-zero, either  $\lambda_1 = 0$  or  $\lambda_2 = 0$

If  $\lambda_1 = 0$ ,  $\xi_1 = \eta_1 = \zeta_1 = 0$ , i.e.,  $(u_1, v_1, w_1)$  is irrotational.

If  $\lambda_2 = 0$ ,  $\xi_2 = \eta_2 = \zeta_2 = 0$ , i.e.,  $(u_2, v_2, w_2)$  is irrotational

If one motion is irrotational, the velocity components of the other must be harmonic.

4 The equations of motion of a viscous homogeneous incompressible fluid are

$$\frac{\partial u}{\partial t} - v\zeta + w\eta = -\frac{\partial \chi'}{\partial x} + \nu \nabla^2 u$$

$$\frac{\partial v}{\partial t} - w\xi + u\zeta = -\frac{\partial \chi'}{\partial y} + \nu \nabla^2 v$$

$$\frac{\partial w}{\partial t} - u\eta + v\xi = -\frac{\partial \chi'}{\partial z} + \nu \nabla^2 w$$

where  $\chi' = \frac{p}{\rho} + \frac{1}{2}q^2 + \Omega$ .

With  $\lambda_1$  and  $\lambda_2$  independent of  $x, y$  and  $z$  these can be written as

$$\frac{\partial u_1}{\partial t} + \nu \lambda_1 \lambda_2 u_1 + \lambda_2 (w_1 v_2 - v_1 w_2) = -\frac{\partial \chi_1'}{\partial x} \quad . \quad . \quad . \quad (1)$$

$$\frac{\partial v_1}{\partial t} + \nu \lambda_1 \lambda_2 v_1 + \lambda_2 (u_1 w_2 - w_1 u_2) = -\frac{\partial \chi_1'}{\partial y} \quad . \quad . \quad . \quad (2)$$

$$\frac{\partial w_1}{\partial t} + \nu \lambda_1 \lambda_2 w_1 + \lambda_2 (v_1 u_2 - u_1 v_2) = -\frac{\partial \chi_1'}{\partial z} \quad . \quad . \quad . \quad (3)$$

and

$$\frac{\partial u_2}{\partial t} + \nu \lambda_1 \lambda_2 u_2 + \lambda_1 (v_1 w_2 - w_1 v_2) = -\frac{\partial X_2'}{\partial x} \quad . \quad . \quad . \quad (4)$$

$$\frac{\partial v_2}{\partial t} + \nu \lambda_1 \lambda_2 v_2 + \lambda_1 (w_1 u_2 - u_1 w_2) = -\frac{\partial X_2'}{\partial y} \quad . \quad . \quad . \quad (5)$$

$$\frac{\partial w_2}{\partial t} + \nu \lambda_1 \lambda_2 w_2 + \lambda_1 (u_1 v_2 - v_1 u_2) = -\frac{\partial X_2'}{\partial z} \quad . \quad . \quad . \quad (6)$$

for the motions  $(u_1, v_1, w_1)$  and  $(u_2, v_2, w_2)$  respectively

Multiplying (1) by  $\lambda_1$  and (4) by  $\lambda_2$  and adding,

$$\lambda_1 \frac{\partial u_1}{\partial t} + \lambda_2 \frac{\partial u_2}{\partial t} + \nu \lambda_1 \lambda_2 (\lambda_1 u_1 + \lambda_2 u_2) = -\frac{\partial \Sigma}{\partial x}$$

where  $\Sigma = \lambda_1 X_1' + \lambda_2 X_2'$ .

Similarly, from (2) and (5), (3) and (6) we get

$$\lambda_1 \frac{\partial v_1}{\partial t} + \lambda_2 \frac{\partial v_2}{\partial t} + \nu \lambda_1 \lambda_2 (\lambda_1 v_1 + \lambda_2 v_2) = -\frac{\partial \Sigma}{\partial y}$$

and  $\lambda_1 \frac{\partial w_1}{\partial t} + \lambda_2 \frac{\partial w_2}{\partial t} + \nu \lambda_1 \lambda_2 (\lambda_1 w_1 + \lambda_2 w_2) = -\frac{\partial \Sigma}{\partial z}$

But  $\frac{\partial \Sigma}{\partial x} dx + \frac{\partial \Sigma}{\partial y} dy + \frac{\partial \Sigma}{\partial z} dz$  must be a perfect differential,

i.e.,  $\frac{\partial^2 \Sigma}{\partial y \partial x} = \frac{\partial^2 \Sigma}{\partial x \partial y}$  etc.

Hence, using I,

$$\lambda_1 \frac{\partial}{\partial t} (\lambda_2 u_2) + \lambda_2 \frac{\partial}{\partial t} (\lambda_1 u_1) + \nu \lambda_1^2 \lambda_2^2 (u_1 + u_2) = 0 \quad . \quad . \quad . \quad (7)$$

with two similar equations in  $v$ 's and  $w$ 's

If the two motions are steady then

(i)  $\nu = 0$ . The fluid is non-viscous.

or (ii)  $\lambda_1 \lambda_2 = 0$ . One of the motions is irrotational.

or (iii)  $u_1 + u_2, v_1 + v_2, w_1 + w_2$  separately vanish.

If  $\lambda_1$  and  $\lambda_2$  are absolute constants, we get from (7) and two allied equations

$$u_1 + u_2 = \Phi_1 e^{-\nu \lambda_1 \lambda_2 t}$$

$$v_1 + v_2 = \Phi_2 e^{-\nu \lambda_1 \lambda_2 t}$$

$$w_1 + w_2 = \Phi_3 e^{-\nu \lambda_1 \lambda_2 t}$$

where  $\Phi_1, \Phi_2, \Phi_3$  are functions of  $x, y$  and  $z$  only.

If either  $\lambda_1$  or  $\lambda_2$  is zero, i.e., if one of the two motions is irrotational, the motion resulting from the superposition of  $(u_1, v_1, w_1)$  upon  $(u_2, v_2, w_2)$  must be steady.

5. Multiplying equations (1), (2), (3) by  $u_1, v_1, w_1$  respectively and adding,

$$\left(\frac{1}{2} \frac{\partial}{\partial t} + \nu \lambda_1 \lambda_2\right) (u_1^2 + v_1^2 + w_1^2) = -u_1 \frac{\partial X_1'}{\partial x} - v_1 \frac{\partial X_1'}{\partial y} - w_1 \frac{\partial X_1'}{\partial z} \quad (8)$$

Multiplying the same equations by  $u_2, v_2, w_2$  respectively and adding,

$$\begin{aligned} u_2 \frac{\partial u_1}{\partial t} + v_2 \frac{\partial v_1}{\partial t} + w_2 \frac{\partial w_1}{\partial t} + \nu \lambda_1 \lambda_2 (u_1 u_2 + v_1 v_2 + w_1 w_2) \\ = -u_2 \frac{\partial X_1'}{\partial x} - v_2 \frac{\partial X_1'}{\partial y} - w_2 \frac{\partial X_1'}{\partial z} \end{aligned} \quad (9)$$

Similarly, from (4), (5) and (6) we get

$$\left(\frac{1}{2} \frac{\partial}{\partial t} + \nu \lambda_1 \lambda_2\right) (u_2^2 + v_2^2 + w_2^2) = -u_2 \frac{\partial X_2'}{\partial x} - v_2 \frac{\partial X_2'}{\partial y} - w_2 \frac{\partial X_2'}{\partial z} \quad (10)$$

and

$$\begin{aligned} u_1 \frac{\partial u_2}{\partial t} + v_1 \frac{\partial v_2}{\partial t} + w_1 \frac{\partial w_2}{\partial t} + \nu \lambda_1 \lambda_2 (u_1 u_2 + v_1 v_2 + w_1 w_2) \\ = -u_1 \frac{\partial X_2'}{\partial x} - v_1 \frac{\partial X_2'}{\partial y} - w_1 \frac{\partial X_2'}{\partial z} \end{aligned} \quad (11)$$

Adding (8), (9), (10) and (11) we get after slight re-arrangement

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \{(u_1 + u_2)^2 + (v_1 + v_2)^2 + (w_1 + w_2)^2\} E \right] \\ = -2 \left\{ (u_1 + u_2) \frac{\partial}{\partial x} + (v_1 + v_2) \frac{\partial}{\partial y} + (w_1 + w_2) \frac{\partial}{\partial z} \right\} (X_1' + X_2') E \end{aligned}$$

where  $E = e^{\nu \lambda_1 \lambda_2 t}$

If  $\lambda_1$  and  $\lambda_2$  are absolute constants, this gives on substituting the values of  $u_1 + u_2, v_1 + v_2, w_1 + w_2$  from the last article.

$$\left( \varphi_1 \frac{\partial}{\partial x} + \varphi_2 \frac{\partial}{\partial y} + \varphi_3 \frac{\partial}{\partial z} \right) (X_1' + X_2') = 0$$

which states that  $X_1' + X_2'$  is constant along the stream lines of the resulting motion at any given instant. The value of the constant depends on the stream lines chosen. But  $X_1' + X_2'$  is the value of  $X'$  for the combined motion.

This therefore can be regarded as an extension of Bernoulli's theorem to a class of unsteady motions of which the stream lines and the vortex lines do not coincide.\*

6. Let us now investigate if there can exist motions of the type I.

For this purpose we assume that  $\lambda_1$  and  $\lambda_2$  are absolute constants and  $w_1$  and  $w_2$  are both zero.

We then have from I and the continuity condition

$$\lambda_1 u_2 = -\frac{\partial v_1}{\partial x}, \lambda_1 v_2 = \frac{\partial u_1}{\partial x}, \frac{\partial v_1}{\partial x} - \frac{\partial u_1}{\partial y} = 0, \frac{\partial u_1}{\partial x} + \frac{\partial v_1}{\partial y} = 0$$

and 
$$\lambda_2 u_1 = -\frac{\partial v_2}{\partial x}, \lambda_2 v_1 = \frac{\partial u_2}{\partial x}, \frac{\partial v_2}{\partial x} - \frac{\partial u_2}{\partial y} = 0, \frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} = 0$$

Solving these we get

$$u_1 = A_1 \sin \Delta + A_2 \cos \Delta$$

$$v_1 = A_3 \sin \Delta + A_4 \cos \Delta$$

and 
$$u_2 = \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} \{A_4 \sin \Delta - A_3 \cos \Delta\}$$

$$v_2 = \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} \{A_1 \cos \Delta - A_2 \sin \Delta\}$$

where  $\Delta = x \sqrt{\lambda_1 \lambda_2}$ , and the A's are functions of  $x, y$  and  $t$  satisfying

$$\frac{\partial A_1}{\partial x} + \frac{\partial A_3}{\partial y} = 0, \frac{\partial A_2}{\partial y} = \frac{\partial A_4}{\partial x}$$

$$\frac{\partial A_3}{\partial x} + \frac{\partial A_4}{\partial y} = 0, \frac{\partial A_1}{\partial y} = \frac{\partial A_2}{\partial x}$$

The equations of motion for  $(u_1, v_1, 0)$  are

$$\frac{\partial u_1}{\partial t} + \nu \lambda_1 \lambda_2 u_1 = -\frac{\partial \chi_1}{\partial x}$$

$$\frac{\partial v_1}{\partial t} + \nu \lambda_1 \lambda_2 v_1 = -\frac{\partial \chi_1}{\partial y}$$

$$\lambda_2 (v_1 u_2 - u_1 v_2) = -\frac{\partial \chi_1}{\partial x}$$

The conditions of integrability of these are

$$\left(\frac{\partial}{\partial t} + \nu \lambda_1 \lambda_2\right) \frac{\partial u_1}{\partial x} = \lambda_2 \frac{\partial}{\partial x} (v_1 u_2 - u_1 v_2)$$

\* Cf. § 6 of the paper 'Superposable Fluid Motions'. . . . *loc. cit.*

and 
$$\left(\frac{\partial}{\partial t} + \nu\lambda_1\lambda_2\right)\frac{\partial v_1}{\partial x} = \lambda_2 \frac{\partial}{\partial y}(v_1u_2 - u_1v_2)$$

From the first of these we get after substituting the values of  $u$ 's and  $v$ 's and rearranging the terms

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \nu\lambda_1\lambda_2\right)(A_1 \cos \Delta - A_2 \sin \Delta) \\ &= \frac{\partial}{\partial x} \left[ \frac{1}{2} \sin 2\Delta (A_2^2 + A_4^2 - A_1^2 - A_3^2) - \cos 2\Delta (A_1A_2 + A_3A_4) \right] \end{aligned}$$

And since  $\Delta$  alone contains  $x$ ,

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \nu\lambda_1\lambda_2\right)(A_1, A_2) = 0 \\ & \frac{\partial}{\partial x}(A_3A_4 + A_1A_2) = 0, \quad \frac{\partial}{\partial x}(A_2^2 + A_4^2 - A_1^2 - A_3^2) = 0 \end{aligned}$$

Similarly, from the second we get

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \nu\lambda_1\lambda_2\right)(A_3, A_4) = 0 \\ & \frac{\partial}{\partial y}(A_3A_4 + A_1A_2) = 0, \quad \frac{\partial}{\partial y}(A_2^2 + A_4^2 - A_1^2 - A_3^2) = 0 \end{aligned}$$

i.e.,  $A_1 = \theta_x e^{-\nu\lambda_1\lambda_2 t}$ ,  $A_2 = \varphi_x e^{-\nu\lambda_1\lambda_2 t}$ ,  $A_3 = \theta_y e^{-\nu\lambda_1\lambda_2 t}$ ,  $A_4 = \varphi_y e^{-\nu\lambda_1\lambda_2 t}$

where  $\theta$  and  $\varphi$  are harmonic functions of  $x$  and  $y$  satisfying

$$\begin{aligned} \theta_x \varphi_x + \theta_y \varphi_y &= c_1 \\ \varphi_x^2 + \varphi_y^2 - \theta_x^2 - \theta_y^2 &= c_2 \end{aligned}$$

where the  $c$ 's are absolute constants

It is easy to see that with these values of the  $A$ 's the equations of motion of  $(u_2, v_2, 0)$  also become integrable

The two superposable motions are therefore

$$\begin{aligned} u_1 &= (\theta_x \sin \Delta + \varphi_x \cos \Delta) e^{-\nu\lambda_1\lambda_2 t} \\ v_1 &= (\theta_y \sin \Delta + \varphi_y \cos \Delta) e^{-\nu\lambda_1\lambda_2 t} \\ w_1 &= 0 \end{aligned}$$

and

$$\begin{aligned} u_2 &= \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} \{\varphi_y \sin \Delta - \theta_y \cos \Delta\} e^{-\nu\lambda_1\lambda_2 t} \\ v_2 &= \left(\frac{\lambda_1}{\lambda_2}\right)^{\frac{1}{2}} \{\theta_x \cos \Delta - \varphi_x \sin \Delta\} e^{-\nu\lambda_1\lambda_2 t} \\ w_2 &= 0 \end{aligned}$$



The above belong to that class of uniplanar motions in which the ratio between the vorticity components of one and the velocity components of the other is the same everywhere at all times. The two motions decay exponentially with time, the decay being rapid for liquids of high kinematic viscosity and slow for liquids of low kinematic viscosity. They cannot vanish in the same plane  $x = \text{constant}$ . That is, the vorticity and velocity of the same motion cannot vanish everywhere in a plane  $x = \text{constant}$ .

The angle which the stream lines of any one motion make with its own vortex lines is

$$\tan^{-1} \left( \frac{c_1 \cos 2\Delta - \frac{1}{2} c_2 \sin 2\Delta}{\theta_x \varphi_y - \varphi_x \theta_y} \right),$$

so that the stream lines are distinct from the vortex lines except for the planes

$$x = \frac{1}{2(\lambda_1 \lambda_2)^{\frac{1}{2}}} \left\{ n\pi + \tan^{-1} \left( \frac{2c_1}{c_2} \right) \right\}, \quad n \text{ being an integer or zero,}$$

in which the two coincide. If this angle becomes a right angle it can be shown that  $\theta_x$ ,  $\theta_y$ ,  $\varphi_x$ ,  $\varphi_y$  must all be constants. The stream lines and the vortex lines then become straight lines lying in planes  $x = \text{constant}$ .

The motions are also self-superposable.\*

\* They satisfy equations (13) of the paper 'Superposable Fluid Motions'

see *cit.*

# THE ROTATING CEPHEID

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It has been shown that a fast rotating star cannot execute purely radial oscillations

In a previous paper<sup>1</sup> we have shown that the superposition of a small amount of rotation does not materially affect the results arrived at for the radial oscillations of a spherical, non-rotating star. The rotation was supposed to be so small that we could take the surface of the star to be a spheroid and that we could neglect terms of the order of  $v^2$  where

$$v = \omega^2 / (2\pi G \rho), \quad (1)$$

where  $\omega$  is the angular velocity of rotation and  $\bar{\rho}$  the mean density of the star. In this paper we shall show that for a somewhat greater angular velocity of rotation so that we can retain terms of the order of  $v^2$ , the oscillations will not remain purely radial. It will be sufficient for our purpose to consider the uniform radial oscillations of a homogeneous spheroid. We make the plausible assumption, as explained in the paper<sup>1</sup> referred to that the spheroidal surface preserves its form (i.e., meridional eccentricity) throughout the oscillation.

Taking the axis of rotation as Z-axis, the equation of oscillatory motion for a rotating star is, in polar coordinates,

$$\frac{d^2\xi}{dt^2} = \frac{\partial V}{\partial \xi} - \frac{1}{\rho} \frac{\partial P}{\partial \xi} + \omega^2 \xi \sin^2 \theta, \quad (2)$$

where  $V$ ,  $P$  and  $\rho$  are respectively the gravitational potential, pressure and density at an internal point  $(\xi, \theta, \phi)$ , and  $\omega$  is the angular velocity of rotation. The term  $\omega^2 \xi \sin^2 \theta$  in (1) is due to the rotation.

We will, as we have said, retain in our equations terms up to the order of  $v^2$ , where  $v$  is defined by (1), that is, up to the order of  $\epsilon^4$ , where  $\epsilon$  is the meridional eccentricity of the spheroid. We will also consider small oscillations so that we will neglect terms of the order of  $\xi_1^3$ , where  $\xi_1$  is the amplitude of the oscillation.

Let  $P$ ,  $\rho$  and  $g$  be the pressure, density and gravity at a point distant  $\xi$  from the centre at any instant of time  $t$  and let the suffix zero denote the undisturbed values of these variables. Let

$$\xi = \xi_0(1 + \xi_1), \quad P = P_0(1 + P_1), \quad \rho = \rho_0(1 + \rho_1), \quad (3)$$

and 
$$\xi_1 = a_1 \cos nt, \quad (4)$$

where the period

$$n = 2\pi/\Pi \quad (5)$$

Following Eddington<sup>1</sup> we will suppose the oscillations to be adiabatic, so that we have the following equation

$$P_1 = \gamma \rho_1, \quad (6)$$

where  $\gamma$  is the effective ratio of the specific heats, regarding the matter and enclosed radiation as one system.

We know that the angular velocity  $\omega$  of rotation is connected with the eccentricity  $e$  of the spheroid by the relation<sup>2</sup>

$$\begin{aligned} \frac{\omega^2}{2\pi G \rho_0} &= \frac{3-2e^2}{e^3} (1-e^2)^{\frac{1}{2}} \sin^{-1} e - 3 \left( \frac{1}{e^3} - 1 \right) \\ &= \frac{1}{15} e^3 + \frac{1}{15} e^5, \end{aligned} \quad (7)$$

retaining terms up to the order of  $e^4$ .

If  $a$  be the semi-major axis of the spheroid, the polar equation of the surface can be put in the form

$$a = r \left\{ 1 + \frac{1}{2} \mu^2 e^2 + \frac{1}{2} \mu^2 e^4 (1 - \frac{1}{2} \mu^2) \right\}, \quad (8)$$

where  $\mu = \cos \theta$  (9)

The potential  $V$  of the homogeneous spheroid of mass  $M$  at an external point distant  $r$  from the centre is given by<sup>3</sup>

$$V = \frac{GM}{r} \left\{ 1 - \frac{3P_2}{3 \cdot 5} \left( \frac{ae}{r} \right)^2 + \frac{3P_4}{5 \cdot 7} \left( \frac{ae}{r} \right)^4 \right\}, \quad (10)$$

where  $P_2$  and  $P_4$  are Legendre coefficients, viz.,

$$P_2 = \frac{1}{2} (3\mu^2 - 1) \text{ and } P_4 = \frac{1}{8} (35\mu^4 - 30\mu^2 + 3) \quad (11)$$

From (10) we have  $g_0$ , the undisturbed value of gravity at the point  $\xi_0$  given by

$$g_0 = \frac{4\pi}{3} G \rho_0 C_1 \xi_0, \quad (12)$$

where 
$$C_1 = 1 + \frac{\mu^2}{5} (3\mu^2 - 1) + \frac{\mu^4}{35} (15\mu^2 - 4) \quad (13)$$

We have the equation of relative equilibrium

$$\frac{1}{\rho_0} \frac{\partial P_0}{\partial \xi_0} = -g_0 + \omega^2 \xi_0 (1 - \mu^2) \quad (14)$$

From (12) and (14) we have by integration the undisturbed value  $P_0$  of the pressure at  $\xi_0$  given by

$$P_0 = \frac{2\pi G}{3} \rho_0^2 C_2 (r^2 - \xi_0^2) \quad (15)$$

where 
$$C_2 = C_1 - \frac{3\omega^2 (1 - \mu^2)}{4\pi G \rho_0} \quad (16)$$

and  $r$  = the radius vector to the surface in the direction  $(\theta, \phi)$

We have shown in the paper referred to<sup>5</sup> that the equation of the conservation of mass will be

$$\rho_0 \xi_0^2 d\xi_0 = \rho \xi^2 d\xi \quad (17)$$

From (3) we have

$$\frac{d\xi}{d\xi_0} = 1 + \xi_1 \quad (18)$$

It should be noted that  $\xi_1$  is independent of  $\xi_0$  in consequence of the assumption of uniform oscillation.<sup>6</sup>

From (8), (17) and (18) we have

$$1 + \rho_1 = \frac{\rho}{\rho_0} = \frac{\xi_0^2}{\xi^2} \frac{d\xi_0}{d\xi} = 1 - 3\xi_1,$$

whence 
$$\rho_1 = -3\xi_1, \quad (19)$$

to the first power of  $\xi_1$ .

From (6) and (14) we have

$$P_1 = -3 \gamma \xi_1 \quad (20)$$

We see that  $P_1$  and  $\rho_1$  are also independent of  $\xi_0$ , since  $\xi_1$  is so. From (2), (3) and (4) we have the equation of oscillatory motion

$$\frac{1}{\rho} \frac{\partial P}{\partial \xi} = -g + \omega^2 \xi \sin^2 \theta + n^2 \xi_0 \xi_1 \quad (21)$$

In consequence of our assumption of uniform expansion and contraction, the spheroid remains homogeneous (though of a different density at each instant) throughout the oscillation, in other words, the density at each point is a function of the time but not of its distance from the centre.

Hence we have from (3), (12) and (19)

$$\frac{g}{g_0} = \frac{\rho}{\rho_0} \frac{\xi}{\xi_0} = (1 + \rho_1) (1 + \xi_1) = (1 - 3 \xi_1) (1 + \xi_1),$$

whence we have

$$g = g_0 (1 - 2 \xi_1). \quad (22)$$

to the first power of  $\xi_1$ .

From (17) we have

$$\rho d\xi = \rho_0 \frac{\xi_0}{\xi_1} d\xi_0 = \rho_0 (1 - 2 \xi_1) d\xi_0 \quad (23)$$

From (21) and (23) we have

$$\frac{1}{\rho_0} \frac{\partial P}{\partial \xi_0} = - (1 - 2 \xi_1) g + n^2 \xi_0 \xi_1 + \omega^2 \xi_0 (1 - \mu^2) (1 - \xi_1) \quad (24)$$

We have from (3), (22) and (24)

$$\frac{1}{\rho_0} \frac{\partial}{\partial \xi_0} (P_0 + P_0 P_1) = - (1 - 4 \xi_1) g_0 + n^2 \xi_0 \xi_1 + \omega^2 (1 - \mu^2) \xi_0 (1 - \xi_1) \quad (25)$$

Equation (25) breaks up into the equation of relative equilibrium (14) and the equation of oscillatory motion

$$\frac{1}{\rho_0} \frac{\partial}{\partial \xi_0} (P_0 P_1) = 4 g_0 \xi_1 + n^2 \xi_0 \xi_1 - \omega^2 (1 - \mu^2) \xi_0 \xi_1 \quad (26)$$

By (20) and (14), equation (26) reduces to

$$\{n^2 \xi_0 + \omega^2 (1 - \mu^2) (3\gamma - 1) \xi_0 - g_0 (3\gamma - 4)\} \xi_1 = 0 \quad (27)$$

As  $\xi_1$  is evidently not zero, we have from (27)

$$n = \frac{\rho_0}{\xi_0} (3\gamma - 4) - \omega^2 (1 - \mu^2)(3\gamma - 1)$$

Hence by (12) we have

$$n^2 = \frac{4\pi}{3} (4\rho_0 C_1 (3\gamma - 4) - \omega^2 (1 - \mu^2) (3\gamma - 1)), \quad (28)$$

where  $C_1$  is given by (13)

If the oscillation be purely radial, the period given by (28) must be independent of  $\mu$ . Hence we must have

$$\frac{4\pi}{3} C_1 \rho_0 (3\gamma - 4) \left( \frac{3e^2}{5} + \frac{12e^4}{35} \right) + \omega^2 (3\gamma - 1) = 0 \quad (29)$$

Substituting (7) in (29) we have

$$\begin{aligned} \gamma &= \frac{1 + \frac{1}{2} e^2}{1 + \frac{1}{5} e^2} \\ &= \frac{14}{15} + \frac{18}{175} e^2 - \frac{108}{2625} e^4 \end{aligned} \quad (30)$$

As  $e^2$  is much less than 1, we see that  $\gamma$  given by (30) is much less than the critical value  $\frac{4}{3}$  and hence that the oscillations cannot be stable. We have further, if (29) be satisfied, that the period will be given by

$$\frac{n^2}{2\pi G \rho_0} = (3\gamma - 4) \left( \frac{2}{3} - \frac{2e^2}{15} - \frac{8e^4}{105} \right) - (3\gamma - 1) \left( \frac{4}{15} e^2 + \frac{4}{105} e^4 \right) \quad (31)$$

Substituting for  $\gamma$  from (30) in (31) we have

$$\frac{n^2}{2\pi G \rho_0} = - \left( \frac{4}{5} + \frac{4}{35} e^2 + \frac{32}{175} e^4 \right) \quad (32)$$

The period given by (32) is imaginary and hence no radial mode of uniform oscillation is possible.

As the star oscillates uniformly in the fundamental mode, this mode cannot be radial, and presumably the same will be the case with the higher modes which, exciting non-uniform oscillations, would disturb the homogeneity of the star. Further a heterogeneous spheroid cannot *a fortiori* oscillate radially, if this be not possible for the homogeneous spheroid. A non-radial oscillation will however meet with material viscosity which will not probably allow it to last long. Our analysis bears out the observational fact of the non-existence of fast-rotating Cepheids.

The author considers it a great privilege to record his sincere thanks to Prof A C Banerji, under whose guidance he has carried out the above investigation

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# THE ARMS OF A SPIRAL NEBULA IN RESISTING MEDIUM II

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It is unlikely on physical grounds apart from the direct astronomical evidence that inter-stellar space is entirely void. Matter may escape from stars by radio active emission, by radiation pressure or by the ordinary loss of high speed molecules. Celestial magnetic storms are usually ascribed to some kind of corpuscular emission from the Sun. Moreover Eddington's<sup>4</sup> theoretical researches as well as Plaskett's<sup>5</sup> and Pearce's<sup>6</sup> observational investigations show that inter-stellar space (within the confines of the galaxy) is not empty but is filled with a very rarefied gas of substantially uniform density. Hence the movement of an ejected particle would be taking place in a resisting medium.

In the first part<sup>1</sup> we considered the resistance varying as  $\frac{v}{r^2}$  and showed that the path is an approximate deformed spiral. In this paper we consider the resistance varying as  $v$  alone say it is equal to  $kv$  where  $k$  is constant and small.

The radial and transverse components are

$$-kr \text{ and } -kr\dot{\theta}$$

Equations of motion now become

$$r - r\dot{\theta}^2 = -f^1 - kr \tag{1}$$

$$\frac{1}{r} \frac{d}{dt} (r^2 \dot{\theta}) = -kr\dot{\theta} \tag{2}$$

Equation (2) gives

$$r^2 \dot{\theta} = h_0 e^{-kt} \tag{3}$$

where  $h_0$  is constant of integration whose value is  $h_0$  when  $t=0$

Put  $r = \frac{1}{u}$   $\therefore -\frac{1}{u^2} \frac{du}{d\theta} h_0 e^{-kt} u^2$

$$= -h_0 e^{-kt} \frac{du}{d\theta}$$



and

$$r = h_0^2 u^2 e^{-2kt} \frac{d^2 u}{d\theta^2} + h h_0 e^{-kt} \frac{du}{d\theta}$$

With the help of these, equation (1) becomes

$$\begin{aligned} \frac{d^2 u}{d\theta^2} + u &= \frac{f}{h_0^2 u^2} e^{2kt} \\ &= \frac{1}{h_0^2} \left[ \Lambda_0 + \Lambda_1 u^2 + \Lambda_{2n} u^{2n} \right] e^{2kt} \end{aligned}$$

Taking  $e$  to be very small, we neglect its 2nd and higher powers  
Hence we have

$$\frac{d^2 u}{d\theta^2} + u = \frac{m u_0}{2} e^{2kt} \quad (4)$$

where  $m$  is +ve small and less than 1,

$$\text{i.e., } m < 1$$

Equation (3) on integration gives

$$\int r^2 d\theta = c_1 - \frac{h_0}{h} e^{-kt}$$

where  $c_1$  is the constant of integration

To the first approximation we can take the value of  $\theta^{(0)}$ , when the particle was free to move

$$\theta = \sin^{-1} \frac{2u - mu_0}{(2-m)u_0}$$

$$\int \frac{1}{u^2} \frac{d\theta}{du} du = c_1 - \frac{h_0}{h} e^{-kt}$$

or

$$\int u^2 \{ (u_0 - u) \{ u + u_0 (1-m) \} \}^{\frac{1}{2}} = c_1 - \frac{h_0}{h} e^{-kt}$$

$$\begin{aligned} \frac{1}{u_0^3 (1-m)} \left[ \frac{m}{(1-m)^{\frac{3}{2}}} \cos h^{-1} \sqrt{\frac{u + u_0 (1-m)}{u (2-m)}} - \sqrt{\frac{(u_0 - u) \{ u + u_0 (1-m) \}}{u}} \right] \\ = c_1 - \frac{h_0}{h} e^{-kt} \end{aligned}$$

If  $u = u_0$  when  $t = 0$

then  $\epsilon = \frac{h_0}{l}$

Hence we have

$$u_0 \frac{1}{l(1-m)} \left[ \frac{m}{(1-m)^{\frac{1}{2}}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} - \sqrt{\frac{(u-u_0)\{u+u_0(1-m)\}}{u}} \right] \\ = \frac{h_0}{l} (1-\epsilon^2)$$

$$\text{or } \epsilon^2 = 1 - \frac{l}{h_0 u_0^{\frac{1}{2}} (1-m)} \left[ \frac{m}{(1-m)^{\frac{1}{2}}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} - \sqrt{\frac{(u_0-u)\{u+u_0(1-m)\}}{u}} \right]$$

$$\epsilon^{2k} = \left[ 1 + \frac{2l}{h_0 u_0^{\frac{1}{2}} (1-m)} \left\{ \frac{m}{(1-m)^{\frac{1}{2}}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} - \sqrt{\frac{(u_0-u)\{u+u_0(1-m)\}}{u}} \right\} \right]^k$$

keeping terms up to  $k$  only

By substituting the value of  $\epsilon^{2k}$  in (4) we have

$$\frac{d^2 u}{d\theta^2} + u = \frac{m u_0}{2} + \frac{m l}{h_0 u_0^{\frac{1}{2}} (1-m)} \left[ \frac{m}{(1-m)^{\frac{1}{2}}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} - \sqrt{\frac{(u_0-u)\{u+u_0(1-m)\}}{u}} \right]$$

$$\left( \frac{du}{d\theta} \right)^2 + u^2 = m u_0 u + \frac{2m^2 l}{h_0 u_0 (1-m)} \left[ u \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} + \frac{u_0 (1-m)^{\frac{1}{2}}}{2} \sin^{-1} \frac{2u-mu_0}{(2-m)u_0} \right]$$

$$\frac{-2ml}{h_0 u_0 (1-m)} \left\{ -2u_0 (1-m)^{\frac{1}{2}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{u(2-m)}} + \frac{u_0 m}{2} \sin^{-1} \frac{2u-mu_0}{(2-m)u_0} + \sqrt{(u_0-u)\{u+u_0(1-m)\}} \right\} + E$$

The value of the constant of integration  $E$  is determined by putting

$$u = u_0, \frac{du}{d\theta} = 0$$

Hence we have

$$\begin{aligned} \left(\frac{1}{\theta}\right)^2 &= m n_0 (u-n) + \frac{2ml}{h_0 n_0 (1-m)^2} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} \\ &+ h_0 (1-m)^{\frac{1}{2}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} - \frac{2ml}{h_0 n_0 (1-m)^2} \sqrt{(u_0-n) \{u+u_0(1-m)\}} \\ &+ u_0^2 - u \\ \left(\frac{du}{d\theta}\right) &= \sqrt{(u-n) \{u+u_0(1-m)\}} \left\{ 1 + \frac{2ml}{h_0 (1-m)^{\frac{1}{2}}} \left\{ \left( \frac{mu}{(1-m)u_0} + 2 \right) \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} \right. \right. \\ &\left. \left. - \frac{2ml}{h_0 n_0 (1-m)^2} \frac{1}{\sqrt{(u_0-n) \{u+u_0(1-m)\}}} \right\}^{\frac{1}{2}} \right\} \end{aligned}$$

or

$$\begin{aligned} \theta + c &= \int \sqrt{(u_0-n) \{u+u_0(1-m)\}} \frac{du}{h_0 (1-m)^{\frac{1}{2}}} - \frac{ml}{h_0 (1-m)^{\frac{1}{2}}} \int \left\{ \left( \frac{mu}{(1-m)u_0} + 2 \right) \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} \right. \\ &\left. + \frac{mk}{h_0 n_0 (1-m)^2} \int (u_0-n) \{u+u_0(1-m)\} \right. \\ &\left. + \frac{2u-mu_0}{(2-m)u_0} - \frac{u^2}{h_0 n_0 (1-m)^2} \left[ \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} \right] \right. \\ &\left. \left\{ \sqrt{(u_0-n) \{u+u_0(1-m)\}} + \frac{mu_0}{(2-m)^{\frac{1}{2}} u_0^2} \sqrt{(u_0-n) \{u+u_0(1-m)\}} \right\} \right. \\ &+ \frac{u_0(1-m)^{\frac{1}{2}}}{2} \left\{ \frac{1}{u_0^2 (2-m)} \log \frac{u}{u_0-n} + \frac{1}{n_0^2 (2-m) (1-m)} \log \frac{u}{u+u_0(1-m)} \right\} \\ &\left. + \frac{mu_0^2 (1-m)^{\frac{1}{2}}}{2(2-m)^{\frac{1}{2}} u_0^2} \left\{ \frac{1}{u_0} \log \frac{u}{u_0-n} - \frac{1}{u_0(1-m)} \log \frac{u}{u+u_0(1-m)} \right\} \right] \\ &- \frac{2ml}{h_0 (1-m)^{\frac{1}{2}}} \left[ \frac{2}{(2-m)^2 u_0^2} \sqrt{(u_0-n) \{u+u_0(1-m)\}} \cos h^{-1} \sqrt{\frac{u+u_0(1-m)}{n(2-m)}} \right. \\ &\left. + \frac{(1-m)^{\frac{1}{2}}}{(2-m)^{\frac{1}{2}} u_0^2} \left\{ \frac{1}{u_0} \log \frac{u}{u_0-n} - \frac{1}{u_0(1-m)} \log \frac{u}{u+u_0(1-m)} \right\} \right] \\ &+ \frac{mk}{h_0 n_0 (1-m)^2} \frac{1}{n_0 (2-m)} \log \frac{u+u_0(1-m)}{u_0-n} \end{aligned}$$

The sum of the coefficients of the terms which become infinite on putting the initial conditions is zero. Hence we are left with finite terms only

$$\theta = \left( \sin^{-1} \frac{2u - mu_0}{(2-m)u_0} - \frac{\pi}{2} \right) + \cos h^{-1} \sqrt{\frac{u + u_0(1-m)}{2-m}} \left\{ - \frac{m^2 l}{h_0 u_0 (1-m)} \right. \\ \left. - \frac{m^2 l}{h_0 u_0 (1-m)} - \frac{m u_0 (2u - mu)}{(2-m)^2 u_0^2} - \frac{2mk (2u - mu)}{h_0 (1-m)^2 (2-m)^2 u_0} \right\} \\ \theta = \left( \sin^{-1} \frac{2u - mu}{(2-m)u_0} - \frac{\pi}{2} \right) - \frac{2ml}{u_0^2 h_0 (1-m)} \cos h^{-1} \sqrt{\frac{u + u_0(1-m)}{2-m}} \\ \sqrt{(u - u_0) \{ u + u_0(1-m) \}}$$

In order to find the approximate curve at a sufficiently great distance we expand the above terms in powers of  $\frac{u}{u_0}$  keeping only terms up to  $\frac{u}{u_0}$  and neglecting the 2nd and higher powers of  $\frac{u}{u_0}$  further we take  $m$  to be very small. Hence  $\frac{m}{2-m}$  is a very small quantity so we neglect 2nd and higher powers of  $\frac{m}{2-m}$ .

Hence we get

$$\theta = \frac{2}{2-m} \frac{u}{u_0} - \left( \frac{2}{2-m} + \frac{\pi}{2} \right) - \frac{2ml}{u(2-m)} \\ u \log \left\{ \frac{\sqrt{u + u_0(1-m)} + \sqrt{(u_0 - u)(1-m)}}{\sqrt{u}} \right\} + \frac{ml}{u(1-m)} \log (2-m) \\ = \frac{u}{u_0} \left[ \frac{2}{2-m} - \frac{2ml}{u(1-m)^2} \right] - \left( \frac{2}{2-m} + \frac{\pi}{2} \right) + \frac{ml}{u(1-m)} \log (2-m) \\ = l_1 \frac{u}{u_0} - k_2$$

where

$$l_1 = \frac{2}{2-m} - \frac{2ml}{u(1-m)^2}$$

and

$$k_2 = \left[ \frac{2}{2-m} + \frac{\pi}{2} - \frac{ml}{u(1-m)^2} \log (2-m) \right].$$

Thus the curve given by  $\theta = k_1 \frac{u}{u_0} - k_2$  is a deformed spiral

In the end I wish to record my respectful thanks to Prof A C Banerji, for his kind interest in my work

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# SOME INFINITE INTEGRALS

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1. In a recent paper\* I have studied the properties of the function

$$f_{\nu}(x) = \sum_{n=0}^{\infty} \frac{(-1)^n \gamma^n + 2\gamma}{2^{\nu+2\gamma} \Gamma(\nu+\gamma+1)} R(\nu) x^n - 1$$

I have shown therein that

$$f_{\nu}(x) = \frac{(\frac{1}{2}x)^{\nu}}{\Gamma(\nu)} \int_0^1 (1-u)^{\nu-1} e^{-\frac{1}{2}x^2 u} du \quad R(\nu) > 0 \quad (1.1)$$

The object of this note is to evaluate a few infinite integrals involving this function

To begin with, we have

$$f_{\nu}(x) = \frac{x^{\nu-2}}{2^{\nu} \Gamma(\nu)} \int_0^{\frac{1}{2}} \left(1 - \frac{t}{x^2}\right)^{\nu-1} e^{-\frac{1}{2}t} dt$$

$$= O(x^{\nu-2}) \text{ for large } x \text{ and } R(\nu) > 0$$

2. We proceed to evaluate the integral

$$I = \int_0^{\infty} x^{\rho-1} f_{\nu}(ax) dx, \quad R(a) > 0$$

which is convergent for  $R(\nu) > 0$ ,  $0 < R(\nu+p) < 2$

We have, by (1.1),

$$I = \frac{a^{\nu}}{2^{\nu} \Gamma(\nu)} \int_0^{\infty} x^{\rho+\nu-1} dx \int_0^1 (1-u)^{\nu-1} e^{-\frac{1}{2}a^2 x^2 u} du$$

\* A Confluent Hypergeometric Function—*Proc. Nat. Ind. Sc., India* VII, (1941), 177–82.

$$= \frac{a^v}{2^v \Gamma(v)} \int_0^1 (1-u)^{v-1} du \int_0^\infty u^{p+1-1} e^{-\frac{1}{2} a^2 x^2} dx$$

a process easily justifiable. Hence

$$\begin{aligned} I &= \frac{2^{p-1}}{a^p} \cdot \frac{\Gamma(\frac{1}{2}p + \frac{1}{2}v)}{\Gamma(v)} \int_0^1 u^{-\frac{1}{2}p - \frac{1}{2}v} (1-u)^{v-1} du \\ &= \frac{2^{p-1}}{a^p} \cdot \frac{\Gamma(\frac{1}{2}p + \frac{1}{2}v)}{\Gamma(v)} \cdot \frac{\Gamma(1 - \frac{1}{2}p - \frac{1}{2}v) \Gamma(v)}{\Gamma(1 - \frac{1}{2}p + \frac{1}{2}v)}. \end{aligned}$$

Thus, we get

$$\begin{aligned} \int_0^\infty x^{p-1} f_v(ax) dx & \quad R(v) > 0, \quad 0 < R(v+p) < 2 \\ &= \frac{2^{p-1} \pi}{a^p \sin(p+v) \frac{\pi}{2}} \cdot \frac{1}{\Gamma(1 - \frac{1}{2}p + \frac{1}{2}v)}. \end{aligned} \quad (2.1)$$

*Particular cases*

(i)  $p=1-v$

$$\int_0^\infty x^{-v} f_v(ax) dx = \frac{a^{v-1} \pi}{2^v \Gamma(v + \frac{1}{2})} \quad R(v) > 0 \quad (2.2)$$

In particular, when  $v=1, \frac{1}{2}$ , this formula assumes the simpler forms

$$\int_0^\infty f_1(ax) \frac{dx}{x} = \sqrt{\pi} \quad (2.3)$$

$$\int_0^\infty f_{\frac{1}{2}}(ax) \frac{dx}{\sqrt{x}} = \sqrt{2a} \quad . \quad . \quad . \quad . \quad . \quad (2.4)$$

(ii)  $p=1$

$$\int_0^\infty f_v(ax) dx = \frac{1}{a} \Gamma(\frac{1}{2} - \frac{1}{2}v) \quad 0 < R(v) < 1 \quad . \quad . \quad . \quad (2.5)$$

For  $\nu = \frac{1}{2}$  this formula becomes

$$\int_0^c f_{\frac{1}{2}}(ax) dx = \frac{1}{a} \Gamma\left(\frac{1}{2}\right) \quad (2.6)$$

(iii)  $p = \nu$

$$\int_0^c x^{\nu-1} f_{\nu}(ax) dx = \frac{2^{\nu-1} \pi}{a^{\nu} \sin \nu \pi} \quad 0 < R(\nu) < 1 \quad (2.7)$$

For  $\nu = \frac{1}{2}$  this formula reduces to (2.4)

(iv)  $p = \nu - 2$

$$\int_0^{\infty} x^{\nu-3} f_{\nu}(ax) dx = \frac{-2^{\nu-3} \pi}{a^{\nu} \sin \nu \pi} \quad 1 < R(\nu) < 2 \quad (2.8)$$

For  $\nu = \frac{3}{2}$  this becomes

$$\int_0^{\infty} x^{-\frac{1}{2}} f_{\frac{3}{2}}(ax) dx = \frac{\sqrt{a\pi}}{2\sqrt{2}} \quad (2.9)$$

### 3 The integral

$$K = \int_0^{\infty} x^{-p} f_{\nu+p+1}(ax) J_{\nu}(bx) dx \quad R(a) > 0, \quad R(b) > 0, \quad R(\nu+p) \geq -1$$

is convergent for  $-1 < R(\nu) < \frac{3}{2}$ . We have, by (1.1),

$$\begin{aligned} K &= \frac{a^{\nu+p+1}}{2^{\nu+p+1} \Gamma(\nu+p+1)} \int_0^{\infty} x^{\nu+1} J_{\nu}(bx) dx \int_0^1 (1-u)^{\nu+p-1} a^2 x^{\nu} du \\ &= \frac{a^{\nu+p+1}}{2^{\nu+p+1} \Gamma(\nu+p+1)} \int_0^1 (1-u)^{\nu+p} du \int_0^{\infty} x^{\nu+1} e^{-\frac{1}{2}a^2 u x^2} J_{\nu}(bx) dx, \end{aligned}$$



a process easily justifiable. Thus, by using Sonine's formula\* we have

$$\begin{aligned} K &= \frac{a^{\rho-\nu-1} b^{\nu}}{2^{\rho} \Gamma(p+\nu+1)} \int_0^1 u^{-\nu-1} (1-u)^{\nu+\rho} e^{-\frac{b^2}{a^2} u} du \\ &= \frac{a^{\rho-\nu-1} b^{\nu}}{2^{\rho} \Gamma(p+\nu+1)} e^{-\frac{b^2}{a^2}} \int_0^{\infty} \frac{t^{\nu+\rho} e^{-\frac{b^2}{a^2} t}}{(1+t)^{\rho+1}} dt \end{aligned}$$

On using a formula given by Whittaker† we get

$$\begin{aligned} \int_0^{\infty} x^{-\rho} f_{\nu+\rho+1}(ax) J_{\nu}(bx) dx &= R(a) > 0, R(b) > 0, R(\nu+\rho) \geq -1, -1 < R(\nu) < \frac{3}{2} \\ &= \left(\frac{a}{2}\right)^{\rho} e^{-\frac{b^2}{2a^2}} W_{-\frac{1}{2}\nu-\rho-\frac{1}{2}, \pm\frac{1}{2}\nu} \left(\frac{b^2}{a^2}\right) \end{aligned} \quad (3.1)$$

*Particular cases*

(i)  $p = -1$

$$\begin{aligned} \int_0^{\infty} x f_{\nu}(ax) J_{\nu}(bx) dx &= \frac{2}{ab} e^{-\frac{b^2}{2a^2}} W_{\frac{1}{2}-\frac{1}{2}\nu, \pm\frac{1}{2}\nu} \left(\frac{b^2}{a^2}\right) \\ &= \frac{2a^{\nu-2}}{b^{\nu}} e^{-\frac{b^2}{2a^2}}, \quad 0 \leq R(\nu) < \frac{3}{2}, \end{aligned} \quad (3.2)$$

on using the formula

$$W_{m+\frac{1}{2}, \pm m}(x) = x^{m+\frac{1}{2}} e^{-\frac{1}{2}x}.$$

For  $\nu = \frac{1}{2}, 1$ , formula (3.2) assumes the following simpler forms.

$$\int_0^{\infty} \sqrt{x} f_{\frac{1}{2}}(ax) \sin bx \, dx = \sqrt{2\pi} a^{-1} e^{-\frac{b^2}{a^2}}, \quad (3.3)$$

$$\int_0^{\infty} x f_1(ax) J_1(bx) dx = \frac{2}{ab} e^{-\frac{b^2}{a^2}}. \quad (3.4)$$

\* G. N. Watson, *Theory of Bessel Functions*—Camb. (1922) §13.3 (4)

† E. T. Whittaker and G. N. Watson, *Modern Analysis*—4th Edition (1927) §16.12

For  $\nu=0$  (3.2) reduces to the familiar formula

$$\int_0^{\infty} x e^{-\frac{1}{2}a^2 x^2} J_0(bx) dx = \frac{2}{a^2} e^{-\frac{b^2}{2a^2}}.$$

(ii)  $p=0$

$$\begin{aligned} \int_0^{\infty} f_{\nu+1}(ax) J_{\nu}(bx) dx & \quad -1 < \Re(\nu) < \frac{3}{2} \\ & = \frac{1}{b} e^{-\frac{b^2}{2a^2}} W_{-\frac{1}{2}\nu-\frac{1}{2}, \pm\frac{1}{2}\nu}\left(\frac{b^2}{a^2}\right) \end{aligned} \quad (3.5)$$

For  $\nu=\pm\frac{1}{2}$  this formula becomes

$$\int_0^{\infty} f_{\frac{1}{2}}(ax) \frac{\sin bx}{\sqrt{x}} dx = \sqrt{\frac{\pi}{2a}} e^{-\frac{b^2}{2a^2}}, \quad (3.6)$$

$$\int_0^{\infty} f_{\frac{1}{2}}(ax) \frac{\cos bx}{\sqrt{x}} dx = \sqrt{\frac{\pi}{a}} e^{-\frac{b^2}{2a^2}} D_{-1}\left(\frac{b}{a}\sqrt{2}\right) \quad (3.7)$$

(iii)  $p=-\frac{1}{2}\nu-\frac{1}{2}$

$$\begin{aligned} \int_0^{\infty} x^{\frac{1}{2}(\nu+1)} f_{\frac{1}{2}(\nu+1)}(ax) J_{\nu}(bx) dx & \quad -1 < \Re(\nu) < \frac{3}{2} \\ & = \frac{2^{\frac{1}{2}\nu+1}}{a^{\frac{1}{2}\nu+1}\sqrt{\pi}} e^{-\frac{b^2}{2a^2}} K_{\frac{1}{2}\nu}\left(\frac{b^2}{2a^2}\right), \end{aligned} \quad (3.8)$$

on using the formula

$$K_{\nu}(x) = \sqrt{\frac{\pi}{2x}} W_{0,\nu}(2x)$$

For  $\nu=1$  this formula reduces to (3.4). For  $\nu=\pm\frac{1}{2}$ , it assumes the simpler forms

$$\int_0^{\infty} x^{\frac{1}{2}} f_{\frac{1}{2}}(ax) \sin bx dx = 2^{\frac{1}{2}} \sqrt{b} a^{-\frac{1}{2}} e^{-\frac{b^2}{2a^2}} K_{\frac{1}{2}}\left(\frac{b^2}{2a^2}\right), \quad (3.9)$$

$$\int_0^{\infty} x^{-\frac{1}{2}} f_{\frac{1}{2}}(ax) \cos bx \, dx = 2^{\frac{1}{2}} \sqrt{b} a^{-\frac{1}{2}} e^{-\frac{b^2}{2a^2}} K_{\frac{1}{2}} \left( \frac{b^2}{2a^2} \right) \quad (3.10)$$

(iv)  $\nu = 1$

$$\begin{aligned} \int_0^{\infty} x^{-p} f_{p+\frac{1}{2}}(ax) J_1(bx) \, dx & \quad -2 \leq R(p) < 0 \\ &= \left( \frac{a}{2} \right)^p \frac{\Gamma(-p)}{b} e^{-\frac{b^2}{2a^2}} k_{-1, p-1} \left( \frac{b^2}{2a^2} \right), \end{aligned} \quad (3.11)$$

on using the formula

$$W_{n, \frac{1}{2}}(2x) = \Gamma(n+1) k_{n, n}(x),$$

where  $k_n(x)$  denotes Bateman's function of order  $n$

For  $p = -1$ , (3.11) becomes (3.4) For  $p = -2$  it reduces to the familiar result

$$\int_0^{\infty} x^2 e^{-\frac{1}{2} a^2 x^2} J_1(bx) \, dx = \frac{4b}{a^4} e^{-\frac{b^2}{2a^2}},$$

on using the formula

$$k_1(x) = 2xe^{-x^2}$$

(v)  $\nu = \frac{1}{2}$

$$\begin{aligned} \int_0^{\infty} x^{-p-1} f_{p+\frac{1}{2}}(ax) \sin bx \, dx & \quad R(p) \geq -\frac{3}{2} \\ &= \sqrt{2\pi} a^{p-\frac{1}{2}} e^{-\frac{b^2}{2a^2}} D_{-1, p-1} \left( \frac{b}{a} \sqrt{2} \right) \end{aligned} \quad (3.12)$$

If we put  $p = -\frac{3}{2}$  in this formula, we arrive at the familiar result

$$\int_0^{\infty} x e^{-\frac{1}{2} a^2 x^2} \sin bx \, dx = \frac{2\sqrt{\pi}}{a^3} b e^{-\frac{b^2}{2a^2}}.$$

For  $p = -\frac{1}{2}$  (3.12) becomes

$$\int_0^{\infty} f_1(ax) \sin bx \, dx = \frac{\sqrt{2\pi}}{a} e^{-\frac{b^2}{2a^2}} D_{-1}\left(\frac{b}{a}\sqrt{2}\right) \quad (3.13)$$

If we put  $p=0$ ,  $-\frac{1}{2}$  in (3.12), we arrive at (3.6) and (3.9) again

(vii)  $\nu = -\frac{1}{2}$

$$\begin{aligned} \int_0^{\infty} x^{-p-\frac{1}{2}} f_{p+\frac{1}{2}}(ax) \cos bx \, dx & \quad R(p) \geq -\frac{1}{2} \\ &= \sqrt{\pi} a^{p-\frac{1}{2}} e^{-\frac{b^2}{2a^2}} D_{-2p-1}\left(\frac{b}{a}\sqrt{2}\right) \end{aligned} \quad (3.14)$$

Putting  $p=0, -\frac{1}{2}$  in this formula, we arrive at (3.7) and (3.10) again. Putting  $p = -\frac{1}{2}$  we get the familiar result

$$\int_0^{\infty} e^{-\frac{1}{2}ax^2} \cos bx \, dx = \frac{\sqrt{\pi}}{a} e^{-\frac{b^2}{a^2}}$$

If we take  $p=\frac{1}{2}$  in (3.14) we get

$$\int_0^{\infty} f_1(ax) \frac{\cos bx}{x} dx = \sqrt{\pi} e^{-\frac{b^2}{2a^2}} D_{-2}\left(\frac{b}{a}\sqrt{2}\right) \quad (3.15)$$

4. In the same way, we can prove the formula

$$\begin{aligned} \int_0^{\infty} f_{\nu}(ax) f_{\nu-1}(bx) \, dx & \quad R(a) > 0, \quad R(b) > 0, \quad 0 < R(\nu) < 1 \\ &= \frac{\Gamma(2-\nu)}{(\nu-1)a^{\nu}} \left\{ \left(1 + \frac{a^2}{b^2}\right)^{\nu-1} - 1 \right\} \end{aligned} \quad (4.1)$$

In particular, we have

$$\int_0^{\infty} f_{\nu}(ax) f_{\nu-1}(ax) \, dx = \frac{\Gamma(2-\nu)}{(\nu-1)a^{\nu}} \left(2^{\nu-1} - 1\right), \quad (4.2)$$

$$\int_0^{\infty} f_{\frac{1}{2}}(ax) f_{-\frac{1}{2}}(ax) \, dx = \sqrt{\frac{\pi}{a}} \left(1 - \frac{1}{\sqrt{2}}\right) \quad (4.3)$$

Likewise, we have

$$\int_0^{\infty} x f_{\frac{1}{2}}(ax) f_{\frac{1}{2}}(bx) dx \quad \operatorname{Re}(a) > 0, \operatorname{Re}(b) > 0, 0 < \operatorname{Re}(v) < 1$$

$$= \frac{2}{a^v} \Gamma(1-v) (a^2 + b^2)^{v-1} \quad (4.4)$$

In particular,

$$\int_0^{\infty} x f_{\frac{1}{2}}(ax) f_{\frac{1}{2}}(bx) dx = \frac{2\sqrt{\pi}}{\sqrt{a(a^2 + b^2)}}, \quad (4.5)$$

$$\int_0^{\infty} x f_{\frac{3}{2}}(ax) dx = \sqrt{2\pi} a^{-\frac{1}{2}} \quad (4.6)$$

$$\int_0^{\infty} x f_{\frac{1}{2}}(x) dx = \sqrt{2\pi}. \quad (4.7)$$

5. It is equally easy to prove the formulae

$$\int_0^{\infty} f_1(ax) \sin \frac{1}{2} bx^2 dx \approx \frac{1}{a} \tan^{-1} \frac{a^2}{b} \quad \operatorname{Re}(a) > 0, \operatorname{Re}(b) > 0, \quad (5.1)$$

$$\int_0^{\infty} f_1(ax) \cos \frac{1}{2} bx^2 dx \approx \frac{1}{2a} \log \left( 1 + \frac{a^4}{b^2} \right) \quad \operatorname{Re}(a) > 0, \operatorname{Re}(b) > 0 \quad (5.2)$$

As particular cases, we have

$$\int_0^{\infty} f_1(ax) \sin \frac{1}{2} a^2 x^2 dx = \frac{\pi}{4a} \quad \operatorname{Re}(a) > 0 \quad (5.3)$$

$$\int_0^{\infty} f_1(ax) \cos \frac{1}{2} a^2 x^2 dx = \frac{1}{2\sqrt{2}} \log 2 \quad \operatorname{Re}(a) > 0 \quad (5.6)$$

# FORMATION OF THE ARMS OF A SPIRAL NEBULA

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Several theories have been put forward to explain the formation of the arms of spiral nebulae, but no existing theory can satisfactorily explain them. This paper contains our humble attempts. The angular velocities have recently been determined by Mayall<sup>3</sup> and Aller. The observations show, when due allowance is made for the uncertainties that the angular velocity decreases with the distance, although the rate of decrease is very small. In the first part of this paper we have taken variable angular velocity and we have also taken Wyse<sup>4</sup> and Mayall's thin disc model.

By making use of zonal harmonics we derive the expression for potential<sup>1</sup>

$$dv = 2\pi\rho dx \left[ \frac{x}{r} + P_2^2(0) \left( \frac{x}{r} \right)^3 + P_4^2(0) \left( \frac{x}{r} \right)^5 + \dots + P_{2n}^2(0) \left( \frac{x}{r} \right)^{2n+1} \right]$$

where

$$P_{2n} = (-1)^n \cdot \frac{1 \cdot 3 \cdot \dots \cdot 2n-1}{2 \cdot 4 \cdot \dots \cdot 2n}$$

Let us assume that the density  $\rho$  at any point in the disc at a distance  $x$  from the centre can be represented by the expression

$$\rho = A + B \left( \frac{x}{R} \right) + C \left( \frac{x}{R} \right)^2$$

where  $R$  is the radius of the disc and for the assumed case

$$\rho_R = 0 \quad \text{i.e., when } x=R, \text{ we have}$$

$$A + B + C = \rho_R = 0$$

$$\begin{aligned} v &= 2\pi \int_0^R \left[ A + B \frac{x}{R} + C \left( \frac{x}{R} \right)^2 \right] \left[ \frac{x}{r} + P_2^2(0) \left( \frac{x}{r} \right)^3 + \dots \right] dx \\ &= 2\pi \left[ \left( \frac{A}{2} + \frac{B}{3} + \frac{C}{8} \right) \frac{R^3}{r} + \left( \frac{A}{4} + \frac{B}{5} + \frac{C}{6} \right) P_2^2(0) \frac{R^4}{r^3} + \dots \right] \end{aligned}$$

To get attraction,  $f$ , we have to find the value of

$$-\frac{dv}{dr},$$

$$-\frac{dv}{dr} = 2\pi \left[ \left( \frac{A}{2} + \frac{B}{3} + \frac{C}{4} \right) \left( \frac{R}{r} \right)^3 + \left( \frac{A}{4} + \frac{B}{5} + \frac{C}{6} \right) 3 \cdot P_2^2(0) \left( \frac{R}{r} \right)^4 + \dots \right]$$

$$= 2\pi \left[ A_1 \left( \frac{R}{r} \right)^3 + A_2 \left( \frac{R}{r} \right)^4 + 3 \cdot P_2^2(0) + \dots \right]$$

where

$$A_1 = \frac{A}{2} + \frac{B}{3} + \frac{C}{4},$$

$$A_2 = \frac{A}{4} + \frac{B}{5} + \frac{C}{6}$$

Now the angular velocity  $\theta$  decreases as the distance increases

$$\theta = \omega + B' \left( \frac{r}{R} \right)$$

where  $B'$  is constant small, and negative

Now we have equations of motion

$$r - r\theta^2 = -2\pi \left[ A_1 \left( \frac{R}{r} \right)^3 + A_2 3 \cdot P_2^2(0) \left( \frac{R}{r} \right)^4 + \dots \right] \quad (1)$$

$$\frac{1}{r} \frac{d}{dt} (r^2 \theta) = 0 \quad (2)$$

Taking equation (1) we have

$$r = r \left( \omega + B' \frac{r}{R} \right)^2 - 2\pi \left[ A_1 \left( \frac{R}{r} \right)^3 + A_2 3 \cdot P_2^2(0) \left( \frac{R}{r} \right)^4 + \dots \right]$$

$$r^3 = r^3 \omega^2 + B'^2 \frac{r^4}{2R^2} + \frac{\omega B' r^3}{R} + 4\pi \left[ A_1 \frac{R^3}{r} + A_2 P_2^2(0) \frac{R^4}{r^2} + \dots \right] + \text{const.}$$

or

$$r^3 = (r^3 - R^3) \omega^2 \left[ 1 + \frac{B_1^2}{2R^3 \omega^2} (r^3 + R^3) + \frac{\omega B'}{R \omega^2} \frac{(r^3 + rR + R^3)}{r + R} - \frac{4\pi R}{2r^3} \left\{ \frac{A_1}{r(r+R)} + A_2 P_2^2(0) \frac{(r^3 + rR + R^3)}{r^2(r+R)} \right\} \right]$$

keeping terms only up to  $P_2^2(0)$

$$r = \omega(r^2 - R^2)^{\frac{1}{2}} \left[ 1 + \frac{B'^2}{2R^2\omega^2} (r^2 + R^2) + \frac{\omega B'}{R\omega^2} \left( \frac{r^2 + rR + R^2}{r + R} \right) - \frac{4\pi R}{\omega^2} \left\{ \frac{A_1}{(r+R)r} + A_2 P_2^2(0) \cdot \frac{r^2 + rR + R^2}{r^2(r+R)} \right\} \right]^{\frac{1}{2}}$$

or

$$\int \frac{1}{\omega(r^2 - R^2)^{\frac{1}{2}}} - \frac{B'^2}{4R^2\omega^2} \frac{r^2 + R^2}{(r^2 - R^2)^{\frac{1}{2}}} - \frac{2}{3} \frac{\omega B'}{R\omega^2} \frac{r^2 + rR + R^2}{(r+R)(r^2 - R^2)^{\frac{1}{2}}} + \frac{2\pi R}{\omega^2} \left\{ \frac{A_1}{r(r+R)(r^2 - R^2)^{\frac{1}{2}}} + A_2 P_2^2(0) \frac{r^2 + rR + R^2}{r^2(r+R)(r^2 - R^2)^{\frac{1}{2}}} \right\} dr = \int dt$$

From equation (2) we have

$$r^2 \theta = \text{constant}$$

$$= k \text{ (say)}$$

$$\text{or } \theta = k \int \frac{1}{r^2} dt$$

$$\begin{aligned} &= \frac{k}{\omega} \left[ \int \frac{dr}{r^2(r^2 - R^2)^{\frac{1}{2}}} - \frac{B'^2}{4R^2\omega^2} \int \frac{(r^2 + R^2) dr}{r^2(r^2 - R^2)^{\frac{1}{2}}} - \frac{2}{3} \frac{B'}{R\omega} \int \frac{(r^2 + rR + R^2) dr}{r^2(r+R)(r^2 - R^2)^{\frac{1}{2}}} \right. \\ &\quad \left. + \frac{2\pi R}{\omega^2} \left\{ A_1 \int \frac{dr}{r^2(r+R)(r^2 - R^2)^{\frac{1}{2}}} + A_2 P_2^2(0) \int \frac{(r^2 + rR + R^2) dr}{r^2(r+R)(r^2 - R^2)^{\frac{1}{2}}} \right\} \right] + \text{const.} \\ &= \frac{k}{\omega} \left[ \frac{\sqrt{r^2 - R^2}}{rR^2} - \frac{B'^2}{4R^2\omega^2} \left\{ \log (r + \sqrt{r^2 - R^2}) + \frac{\sqrt{r^2 - R^2}}{r} \right\} - \frac{2}{3} \frac{B'}{R^2\omega} \right. \\ &\quad \left. \left\{ \frac{\sqrt{r^2 - R^2}}{r} + \sqrt{\frac{r-R}{r+R}} \right\} - \frac{2\pi R}{\omega^2 R^2} \left\{ A_1 \left\{ \frac{(2r-R)(r^2 - R^2)^{\frac{1}{2}}}{2r^2} + \frac{1}{2} \sin^{-1} \frac{R}{r} \right. \right. \right. \\ &\quad \left. \left. + \sqrt{\frac{r-R}{r+R}} \right\} + A_2 P_2^2(0) \left[ \frac{(2r-R)(r^2 - R^2)^{\frac{1}{2}}}{2r^2} + \frac{(-2R^2 + 3Rr - 10r^2)(r^2 - R^2)^{\frac{1}{2}}}{6r^3} \right. \right. \\ &\quad \left. \left. + \frac{(-6R^3 + 8R^2r - 21Rr^2 + 40r^3)}{24r^3} \frac{(r^2 - R^2)^{\frac{1}{2}}}{r} + \frac{15}{8} \sin^{-1} \frac{R}{r} + \sqrt{\frac{r-R}{r+R}} \right\} \right] + \text{const} \end{aligned}$$

To know the approximate motion of the particle at a sufficiently great distance



we expand the above in powers of  $\frac{R}{r}$  neglecting 2nd and higher powers of  $\frac{R}{r}$ , we have

$$\begin{aligned} \theta = & \frac{k}{\omega R^2} \left[ \frac{\sqrt{r^2 - R^2}}{r} - \frac{B_1}{4\omega^2} \left\{ \log(r + \sqrt{r^2 - R^2}) - \log R + \frac{(r^2 - R^2)^{\frac{1}{2}}}{r} \right\} \right. \\ & - \frac{2}{3} \frac{B'}{\omega} \left\{ \frac{(r^2 - R^2)^{\frac{1}{2}}}{r} + \sqrt{r - R} \right\} - \frac{2\pi R}{\omega^2 R^2} \left\{ A_1 \frac{[(2r - R)(r^2 - R^2)^{\frac{1}{2}}]}{2r^2} + \frac{3}{2} \sin^{-1} \frac{R}{r} \right. \\ & - \frac{3}{2} \frac{\pi}{2} + \sqrt{\frac{r - R}{r + R}} \left. \right\} + \frac{A_2}{4} \left[ \frac{(2r - R)(r^2 - R^2)^{\frac{1}{2}}}{2r^2} + \frac{(-2R^2 + 3Rr - 10r^2)(r^2 - R^2)^{\frac{1}{2}}}{6r^2} \right. \\ & \left. \left. + \frac{(-6R^3 + 8R^2r - 21Rr^2 + 40r^3)}{24r^3} \frac{(r^2 - R^2)^{\frac{1}{2}}}{r} + \frac{15}{8} \sin^{-1} \frac{R}{r} - \frac{15}{8} \frac{\pi}{2} + \sqrt{\frac{r - R}{r + R}} \right] \right] \\ \theta = & k_1 \frac{R}{r} - k_2 \end{aligned}$$

The measurements of V pählem have established that the arms of normal spiral nebula are approximately equiangular spirals over a large part of their length. I have shown above that the gravitational force alone cannot form equiangular spirals hence we cannot suppose that the motions take place under gravitation alone. Hence we look for some other data. Van Maanen's<sup>2</sup> measurements have shown that the velocity increases on passing outwards nebula. As a consequence the particle describes an orbit of ever-increasing radius with ever-increasing velocity.

We note from Oort's formula<sup>6</sup> for the effect of galactic rotation on radial velocities that the radial velocity  $P$  due to differential rotation is proportional to  $r$

$$P = r A \sin 2(G - G_0) \cos^2 \theta$$

when  $A$  is Oort's constant

Hence radial velocity increases with distance which is in accordance with the observational fact of Von Maanen

$$\text{velocity} = \sqrt{r^2 + r'^2 \theta^2} = kr$$

where  $\theta' = \omega$  (angular velocity, constant) and  $\theta = \omega t$

$$r'^2 + r'^2 \theta^2 = k^2 r^2$$

$$r'^2 = r^2 (k^2 - \omega^2)$$

$$\int \frac{dr}{r} = (k^2 - \omega^2)^{\frac{1}{2}} t + \text{const.}$$

$$\begin{aligned}
 r &= A e^{k^2 t - \omega^2 t^2} \\
 &= A e^{\omega^2 t \left( \frac{k^2}{\omega^2} - 1 \right)} \\
 &= A e^{\theta \left( \frac{k^2}{\omega^2} - 1 \right)} \\
 &= A e^{\theta \tan \alpha}
 \end{aligned}$$

which gives an equiangular spiral of angle  $\alpha$  where  $\alpha = \tan^{-1} \left( \frac{k^2}{\omega^2} - 1 \right)^{\frac{1}{2}}$ . It has been observed that two convolutions in their orbits being formed by each nebula an explanation for the finite length of the spiral arms however is given by D. N. Moghe<sup>5</sup> on the basis of finite number of ejecta's of particles. The present author thinks that as the space outside a nebula is not totally devoid of matter the particle will experience some resistance due to which it may only move a finite length.

#### SUMMARY AND CONCLUSIONS

In the first part of this paper variable angular velocity is taken into account and it is shown that the gravitational force alone cannot form equiangular spirals. In the second part we have shown that the equiangular spirals are formed if the effect of the galactic rotation on radial velocity is taken into account i.e. radial velocity due to the differential rotation is proportional to the distance.

In the end I think it my great privilege to record my grateful thanks to Prof. A. C. Banerji for his keen interest in preparation of this paper.

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# LARGE RADIAL OSCILLATIONS OF A STAR

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Assuming a polynomial form for the distribution of density inside a star it has been shown that the stellar model is incapable of large radial oscillations. The analysis confirms Banerji's Cepheid theory of the origin of the solar system, in which an oscillating Cepheid is supposed to break up under the gravitational influence of a passing star.

By large radial oscillations of a star we mean cases in which we have to take into account the square of the amplitude in our equations of oscillatory motion. Most of the workers, following Eddington,<sup>4</sup> have considered small oscillations, so that the square of the amplitude could be neglected. A. C. Banerji has been the first to retain the square of the amplitude in his differential equations. He has considered the following stellar models:

- (1) The star of uniform density, and
- (2) the star with a small, homogeneous core, and the density in the annulus varying inversely as the  $p$ th power of the distance from the centre, where  $p$  is any positive integer excluding 1 and 3.

Banerji has shown his models to be unstable for large radial oscillations, and on this basis has given his entirely novel Cepheid theory of the origin of the solar system.

Sterne<sup>5</sup> has considered the small oscillations of the following three stellar models:

- (1) The star of uniform density,
- (2) the star in which the density varies inversely as the square of the distance from the centre, and
- (3) the star in which nearly all the mass is contained in a particle at the centre and in the rest of the star the density varies inversely as the square of the distance from the centre.

Instability for large radial oscillations of Sterne's model (1) has been shown by Banerji,<sup>1</sup> and of Sterne's models (2) and (3) by P. L. Bhatnagar in his unpublished thesis for the D. Phil. degree of the Allahabad University. As illustrative of the method followed in the general case, alternative proofs have

been given in this paper of the instability for large radial oscillations of Sterne's models (2) and (3)

Any law for which the density varies inversely as some power of the distance from the centre leads to singularities at the centre. Banerji has avoided it by assuming a core of uniform density at the centre. Another way to avoid the singularity would be to assume a polynomial form for the distribution of the density inside a star. This has been done in this paper, and the stellar model shown incapable of large radial oscillations. Inasmuch as the variation of density in any model can be approximated to as closely as desired by a polynomial, the present investigation shows that a star cannot execute purely radial oscillations of large amplitude. The analysis confirms Banerji's Cepheid theory<sup>1</sup> of the origin of the solar system, in which an oscillating Cepheid is supposed to break up under the gravitational influence of a passing star.

Let  $P_0$ ,  $\rho_0$  and  $q_0$  be the undisturbed values of the density, pressure and gravity at a point distant initially  $\xi_0$  from the centre, and the period be  $2\pi/n'$ . Let  $\gamma$  be the effective ratio of the specific heats<sup>2</sup> (regarding the matter and enclosed radiation as one system) so that  $\gamma$  satisfies the differential equation:  $\delta P/P_0 = \gamma \delta \rho/\rho_0$ .

Assuming the following form for the amplitude  $\xi_1$  (after Eddington),<sup>3</sup> viz.,  $\xi_1 = a_1 \cos n't - a_2 \cos \gamma n't - a_3$  where  $a_2$  and  $a_3$  are of order  $a_1^2$ , Banerji<sup>1</sup> has obtained the following equations of oscillatory motion

$$\frac{d^2 a_1}{d\xi_0^2} + \frac{1-\gamma}{\xi_0} \frac{da_1}{d\xi_0} + \left[ \frac{n'^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] a_1 = 0 \quad (1)$$

$$\frac{d^2 a_2}{d\xi_0^2} + \frac{1-\gamma}{\xi_0} \frac{da_2}{d\xi_0} + \left[ \frac{4n'^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] a_2 = \Lambda_1 \quad (2)$$

$$\text{and} \quad \frac{d^2 a_3}{d\xi_0^2} + \frac{1-\gamma}{\xi_0} \frac{da_3}{d\xi_0} - \frac{\alpha \nu}{\xi_0^2} a_3 = \Lambda_1, \quad (3)$$

$$\text{where} \quad \nu = q_0 \rho_0 \xi_0 / P_0, \quad \alpha = 3 - 4/\gamma \quad (4)$$

$$\text{and} \quad \Lambda_1 = \left[ \frac{1}{2} (3\gamma - 1) \frac{n'^2 \rho_0}{P_0 \gamma} - \frac{1}{2} (\gamma - 1) \frac{\alpha \nu}{\xi_0^2} \right] a_1^2 + \frac{1}{2} (\gamma + 1)$$

$$\left[ \frac{n'^2 \rho_0}{P_0 \gamma} - \frac{\alpha \nu}{\xi_0^2} \right] \xi_0 a_1 \frac{da_1}{d\xi_0} + \{1 - \frac{1}{2} (\gamma + 1) \gamma\} \left( \frac{da_1}{d\xi_0} \right)^2 = 0 \quad (5)$$

Let the undisturbed value of density  $\rho_0$  at the point  $\xi_0$  be given by

$$\rho_0 = \sum_0^p \alpha_m \xi_0^m, \quad \dots \quad (6)$$

where  $p$  is a positive integer

We make the usual assumptions that the pressure and the density vanish on the surface, initially of radius  $R$  so that

$$\sum_0^p \alpha_m R^m = 0, \quad (7)$$

and that there is a negative density gradient throughout from the centre of the star right up to its boundary

We have for the value of gravity at  $\xi_0$

$$g_0 = \frac{G}{\xi} \cdot \int_0^{\xi_0} 4\pi \xi_0^2 \rho_0 d\xi_0 - 4\pi G \sum_0^f \alpha_m \frac{R^{m+1} x^{m+1}}{m+3} \quad (8)$$

$$\text{where} \quad \xi_0 = R x \quad (9)$$

The pressure at  $\xi_0$  is given by

$$\begin{aligned} P_0 &= \int_{\xi_0}^R \rho_0 d\xi_0 \\ &= 4\pi G \left\{ \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(m+n+2)} R^{m+n+2} (1-x^{m+n+2}) \right\} \end{aligned} \quad (10)$$

from (6), (8) and (9)

From (4) we have

$$v = \frac{\sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} x^{m+n+2}}{\sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(m+n+2)} R^{m+n+2} (1-x^{m+n+2})} \quad (11)$$

Eliminating  $\alpha_n$  from the numerator of (11) by (7), we have

$$v = - \frac{\sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} \left( \sum_{l=1}^p x^{m+l+1} \right)}{\sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(m+n+2)} R^{m+n+2} \left( \sum_{l=0}^{m+n+1} x^l \right)} \quad (12)$$

cancelling the common factor  $1-x$

Also from (6), (7) and (10) we have

$$\frac{\rho_0}{P_0} = - \frac{\sum_{n=1}^p a_n R^n \sum_{l=0}^{n-1} x^l}{4\pi G \sum_0^p \sum_0^p \frac{a_m a_n}{(m+3)(m+n+2)} R^{m+n+2} \left( \sum_{l=0}^{m+n+1} x^l \right)} \quad (13)$$

again cancelling the common factor  $1-x$

With the substitution (9), the differential equation (1) becomes

$$\frac{d^2 a_1}{dx^2} + \frac{4-v}{x} \frac{da_1}{dx} + \left\{ R^2 \frac{\rho_0}{P_0} - \frac{av}{r} \right\} a_1 = 0 \quad (14)$$

On substituting (12) and (13) in (14), the differential equation (1) further reduces to

$$\begin{aligned} & \left[ \sum_0^p \sum_0^p \frac{a_m a_n}{(m+3)(m+n+2)} R^{m+n+2} \left( \sum_{l=1}^{m+n+2} x^l \right) \right] \frac{d^2 a_1}{dx^2} \\ & + \left[ 4 \sum_0^p \sum_0^p \frac{a_m a_n}{(m+3)(m+n+2)} R^{m+n+2} \left( \sum_0^{m+n+1} x^l \right) + \sum_{n=1}^p \sum_{m=0}^p \frac{a_m a_n}{m+3} R^{m+n+2} \right. \\ & \quad \left. \left( \sum_{l=1}^n x^{m+l+1} \right) \right] \frac{da_1}{dx} \\ & - \left[ \frac{R^2 \rho_0}{4\pi G \gamma} \left( \sum_1^p a_n R^n \sum_1^n x^l - a \sum_{n=1}^p \sum_{m=0}^1 \frac{a_m a_n}{m+3} R^{m+n+2} \left( \sum_1^n x^{m+l} \right) \right) \right] a_1 = 0 \quad (15) \end{aligned}$$

The equation (15) has regular singularities<sup>2</sup> at  $x=0$  and  $x=1$

Assuming

$$a_1 = x^q \sum_0^\infty b_\lambda x^\lambda \quad (16)$$

as a solution in series of (15) and equating the coefficient of  $x^{q-1}$  we have the following indicial equation<sup>3</sup>

$$\begin{aligned} & \sum_0^p \sum_0^p \frac{a_m a_n}{(m+3)(m+n+2)} R^{m+n+2} b_0 q (q-1) + 4 \sum_0^p \sum_0^p \frac{a_m a_n}{(m+3)(m+n+2)} \\ & R^{m+n+2} b_0 q = 0, \quad (17) \end{aligned}$$

which gives  $q=0$  or  $-3$

We reject the negative value to avoid singularity at the centre. With  $q=0$ , (16) becomes

$$a_1 = \sum_0^\infty b_\lambda x^\lambda \quad . \quad . \quad . \quad (18)$$

Substituting (18) in (15) and equating the coefficient of  $x^\lambda$ , we have the recurrence formula

$$\begin{aligned}
 & \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=1}^{m+n+2} (\lambda-l+2)(\lambda-l+1) b_{\lambda-l+2} \right\} \\
 & + 4 \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=0}^{m+n+1} (\lambda-l+1) b_{\lambda-l+1} \right\} \\
 & + \sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{(m+3)} R^{m+n+2} \left\{ \sum_{l=1}^n (\lambda-m-l) b_{\lambda-m-l} \right\} \\
 & - \frac{R^2 n'^2}{4\pi G \gamma} \sum_{n=1}^p \alpha_n R^n \sum_{l=1}^n b_{\lambda-l} + \alpha \sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} \left\{ \sum_{l=1}^n b_{\lambda-m-l} \right\} \\
 & = 0
 \end{aligned} \tag{19}$$

Equation (19) can be put in the form

$$\begin{aligned}
 & \lambda^2 \left[ \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=1}^{m+n+2} b_{\lambda-l+1} \right\} \right] \\
 & \lambda \left[ \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=1}^{m+n+2} (3-2l) b_{\lambda-l+2} \right\} \right] \\
 & + 4 \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=0}^{m+n+1} b_{\lambda-l+1} \right\} \\
 & + \sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} \left\{ \sum_{l=1}^n b_{\lambda-m-l} \right\} \\
 & + \left[ \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=1}^{m+n+2} (2-l)(1-l) b_{\lambda-l+2} \right\} \right] \\
 & + 4 \sum_0^p \sum_0^p \frac{\alpha_m \alpha_n}{(m+3)(n+2)} R^{m+n+2} \left\{ \sum_{l=0}^{m+n+1} (1-l) b_{\lambda-l+1} \right\} \\
 & - \sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} \left\{ \sum_{l=1}^n (l+m) b_{\lambda-m-l} \right\} \\
 & - \frac{R^2 n'^2}{4\pi G \gamma} \sum_{n=1}^p \alpha_n R^n \sum_{l=1}^n b_{\lambda-l} + \alpha \sum_{n=1}^p \sum_{m=0}^p \frac{\alpha_m \alpha_n}{m+3} R^{m+n+2} \left\{ \sum_{l=1}^n b_{\lambda-m-l} \right\} \\
 & = 0
 \end{aligned} \tag{20}$$

Dividing (20) by  $\lambda^2 b_{\lambda-2\rho}$ , and proceeding to the limit as  $\lambda \rightarrow \infty$ , we have

$$\sum_0^{\rho} \sum_0^{\rho} \frac{a_m a_n}{(m+3)(n+u+2)} R^{m+n+2} \left\{ \sum_{l=1}^{m+n+2} L_{l \rightarrow \infty} \left[ \frac{b_{\lambda-l+2}}{b_{\lambda-2\rho}} \right] - 1 \right\} \quad (21)$$

We can easily see that equation (21) is satisfied when

$$L_{l \rightarrow \infty} b_{\lambda-l+2}/b_{\lambda-1} = 1, \quad (22)$$

for then we have

$$L_{l \rightarrow \infty} b_{\lambda-l+2}/b_{\lambda-n} = 1, \quad (23)$$

where  $m$  and  $n$  are any positive integers.

With the substitution (23) the left-hand side of (21) becomes

$$\begin{aligned} \sum_0^{\rho} \sum_0^{\rho} \frac{a_m a_n}{m+3} R^{m+n+2} &= \left\{ \sum_0^{\rho} \frac{a_m}{m+3} R^{m+2} \right\} \left\{ \sum_0^{\rho} a_n R^n \right\} \\ &= 0, \text{ by (7)} \end{aligned}$$

The equation (22) gives unit radius of convergence for the power series (18). This also follows from the general theory<sup>1</sup> of linear differential equations having regular singularities, as the power series (18) about the origin is convergent up to the next nearest singularity of (15), which is, as we have already noted, at the boundary of the star, that is, at  $x=1$ .

We shall now proceed to test the convergence of (18) for  $x=1$ , which is a regular singularity for the differential equation (15). We shall first suppose that the series solution (18) does not terminate.

From (22) we have all the terms to be ultimately of the same sign, and we can put

$$\frac{b_{\lambda}}{b_{\lambda-1}} = 1 - \frac{\epsilon}{\lambda^s}, \quad (24)$$

to the first order of small quantities, where  $\epsilon$  and  $s$  are finite positive quantities.

From (24) we have

$$\frac{b_{\lambda}}{b_{\lambda-m}} = \frac{b_{\lambda}}{b_{\lambda-1}} \frac{b_{\lambda-1}}{b_{\lambda-2}} \cdots \frac{b_{\lambda-m+1}}{b_{\lambda-m}} = 1 - \frac{m\epsilon}{\lambda^s}, \quad (25)$$

to the first order



Dividing (20) by  $b_{\lambda-2\rho}$  and substituting (25) we have, on equating to zero the terms of the highest order,

$$\lambda^2 \sum_0^p \sum_0^p \frac{a_n a_r}{(m+3)(m+n+2)} R^{m+n+2} \sum_{l=1}^{m+n+2} \{l-2\rho-2\} \frac{c}{\lambda^3} + k = 0 \quad (26)$$

where  $l$  is a finite quantity obtained from the terms independent of  $\lambda$  in (20)

Equation (26) with the help of (i) simplifies to

$$\frac{c}{\lambda^3} + \sum_0^p \sum_0^p \frac{m n a_n a_r}{2(m+3)} R^{m+n+2} + k = 0, \quad (27)$$

Now from (8) we have the undisturbed value of gravity on the surface of the star

$$= 4\pi G \sum_0^p \frac{a_m}{m+3} R^{m+1} = \frac{GM}{R^2}$$

where  $M$  is the mass of the star

Hence we have

$$\sum_0^p \frac{a_m}{m+3} R^{m+1} = \frac{M}{4\pi R^2} \quad (28)$$

Also we have from (6) by differentiation

$$\sum_0^p n a_n R^{n-1} = \left( \frac{d\rho_0}{d\xi_0} \right)_{\xi_0=R} \quad (29)$$

Equation (27) with the help of (28) and (29) reduces to

$$\frac{M}{8\pi} \left( \frac{d\rho_0}{d\xi_0} \right)_{\xi_0=R} \frac{c}{\lambda^{2-2\rho}} + k = 0 \quad (30)$$

We have assumed the existence of a negative density gradient throughout the star. Also we have assumed  $c$  in (24) not to be zero, otherwise the series solution (16) would be divergent. Hence the coefficient of  $1/\lambda^{1-2\rho}$  in (30) is not zero.  $k$  cannot be therefore equal to zero, and we must have  $s=2$  in order that equation (30) may be satisfied.

Hence we have from (24)

$$\frac{b_{\lambda-1}}{b_{\lambda+1}} = 1 + \frac{c}{\lambda^2}, \quad (31)$$

to the first order of small quantities where  $c$  is a finite positive quantity. From (31) we have

$$\lim_{\lambda \rightarrow \infty} \lambda(b_\lambda/b_{\lambda+1} - 1) = 0 \quad (32)$$

The series solution (18) is therefore divergent<sup>2</sup> for  $x=1$ .

By an extension of Abel's theorem to series divergent on the circle of convergence we have

$$\lim_{x \rightarrow 1} \sum_{\lambda=0}^{\infty} b_\lambda x^\lambda = \sum_{\lambda=0}^{\infty} b_\lambda = \infty \quad (33)$$

Thus the amplitude of the oscillations increases without limit as we approach the surface of the star and the model in question is therefore unstable for radial oscillations provided as we have supposed that the series solution (18) does not terminate. Hence for stable oscillations (19) must reduce to a finite polynomial.

We shall now consider the complementary function of (2). It can be proved by similar reasoning that this must be a finite polynomial in order that  $a_2$  may be finite on the boundary of the star. As  $a_1$  has been assumed to be a finite polynomial the coefficients of the particular integral of (2) must ultimately satisfy the same recurrence formula as those of the complementary function of (2) and therefore the particular integral of (2) must form a terminating series. Hence  $a_2$  given by (2) must also be a finite polynomial. We can prove similarly that  $a_3$  given by (3) must also be a finite polynomial.

Thus we have that in order that the amplitude  $\xi$  may be finite on the boundary of the star  $a_1$ ,  $a_2$  and  $a$  given by (1), (2) and (3) must be simultaneously terminating polynomials. This is indeed impossible inasmuch as we have only two disposable constants  $n'$  (proportional to frequency of oscillation) and  $\alpha$  given by (4). Further  $\alpha$  is restricted to values between 0 and 6 as  $\gamma$  can only lie between the values  $4/3$  and  $5/3$ . The complementary functions of (2) and (3) are, in fact, obtained from the solution of (1) by changing  $n'$  into  $2n'$  and 0 respectively.

The amplitude therefore cannot remain finite on the boundary of the star and we arrive at the conclusion that the model in question cannot execute radial oscillations of large amplitude.

In conclusion we shall consider particular laws of density to illustrate how the instability arises in the general case considered above.

#### *Particular density laws*

(1) *Sterne's model* (2) viz the star in which the density varies inversely as the square of the distance from the centre<sup>3</sup>

It can be shewn that the differential equations (1), (2) and (3) reduce respectively in this case to

$$(1-x^2) \frac{d^2 a_1}{dx^2} + \frac{2-4x^2}{x} \frac{da_1}{dx} + (\beta x^2 - 2\alpha) \frac{a_1}{x^2} = 0, \quad (34)$$

$$(1-x^2) \frac{d^2 a_2}{dx^2} + \frac{2-4x^2}{x} \frac{da_2}{dx} + (4\beta x^2 - 2\alpha) \frac{a_2}{x^2} = A_1, \quad (35)$$

and 
$$(1-x^2) \frac{d^2 a_3}{dx^2} + \frac{2-4x^2}{x} \frac{da_3}{dx} - \frac{2\alpha}{x^2} a_3 = A_{11}, \quad (36)$$

where 
$$A_1 = \left[ \frac{1}{2} (3\gamma - 1) \beta - \frac{3}{2} (\gamma - 1) \frac{\alpha}{x^2} \right] a_1' + \frac{1}{2} (\gamma + 1) x \left[ \beta - \frac{2\alpha}{x^2} \right] a_1 \frac{da_1}{dx} + \left[ \frac{1}{2} (\gamma - 1) - x^2 \right] \left( \frac{da_1}{dx} \right)^2, \quad (37)$$

and 
$$\beta = 3n'^2 / (2\pi G \gamma \rho), \quad (38)$$

$\bar{\rho}$  being the mean density

The roots of the indicial equation for (34) are  $q = \frac{1}{2} [-1 \pm \sqrt{1 + 8\alpha}]$ . We shall take for  $q$  only the value  $\frac{1}{2} [-1 + \sqrt{1 + 8\alpha}]$  to avoid singularity at the centre. The recurrence formula for the coefficients is

$$b_{2\lambda+2} = b_{2\lambda} \frac{(2\lambda+q)(2\lambda+q+3) - \beta}{(2\lambda+q+1)(2\lambda+q+3) - 2\alpha}. \quad (39)$$

It can be shewn that the amplitude will be infinite at the boundary of the star unless the series solution for  $a_1$  terminates. We have from (39) that the series solution for  $a_1$  will terminate provided

$$\beta = (2\lambda+q)(2\lambda+q+3) \quad (40)$$

We can shew similarly from (35) and (36) that for finite values of  $a_2$  and  $a_3$  on the boundary of the star, the following conditions must be satisfied

$$4\beta = (2\lambda+q)(2\lambda+q+3) \quad (41)$$

and 
$$(2\lambda+q)(2\lambda+q+3) = 0 \quad (42)$$

It is evident that (40), (41) and (42) are simultaneously satisfied when  $\lambda = q = \beta = 0$ . In this case we have from (38) that  $n' = 0$ , or the period of oscillation is infinite, that is, the star is in neutral equilibrium. This also follows from

(4), inasmuch as  $\gamma$  in this case is equal to  $4/3$ , as  $\alpha=0$  when  $q=0$ . We know<sup>6</sup> that  $\gamma$  must exceed  $4/3$  for a stable equilibrium configuration to be possible.

The model therefore cannot execute stable radial oscillations of large amplitude.

(2) Sterne's<sup>8</sup> model (3), *mx*, the star in which nearly all the mass is contained in a particle at the centre, and in the rest of the star the density varies inversely as the square of the distance from the centre.

The differential equations (1), (2) and (3) reduce in this case respectively to

$$(1-x^3) \frac{d^2 a_1}{dx^2} + \frac{1-4x^3}{x} \frac{da_1}{dx} + (\beta x^3 - 3\alpha) \frac{a_1}{x} = 0, \quad (43)$$

$$(1-x^3) \frac{d^2 a_2}{dx^2} + \frac{1-4x^3}{x} \frac{da_2}{dx} + (4\beta x^3 - 3\alpha) \frac{a_2}{x} = A_1, \quad (44)$$

and 
$$(1-x^3) \frac{d^2 a_3}{dx^2} + \frac{1-1x^3}{x} \frac{da_3}{dx} - 3\alpha \frac{a_3}{x} = A_1, \quad (45)$$

where 
$$A_1 = \left[ \frac{1}{2}(3\gamma-1) \beta x^3 - \frac{1}{4} \alpha (\gamma-1) \right] \frac{a_1^2}{x^2} + \frac{1}{2}(\gamma+1)(\beta x^3 - 3\alpha) \frac{a_1}{x} \frac{da_1}{dx} + \frac{1}{2} \left[ (1-3\gamma) - x^3 \right] \left( \frac{da_1}{dx} \right)^2 \quad (46)$$

and 
$$\beta = 9m'^2 / (4\pi(\gamma\rho)) \quad (47)$$

The roots of the indicial equation  $r$  for (43) are  $q = \pm \sqrt{3\alpha}$ . We take only the positive value of  $q$  to avoid singularity at the centre. The recurrence formula for the coefficients is

$$b_{3\lambda+3} = b_{3\lambda} \frac{(3\lambda+q)(3\lambda+q+3)-\beta}{(3\lambda+q+3)^2-3\alpha} \quad (48)$$

From this we deduce as in the previous case that  $a_1$  will be finite provided

$$\beta = (3\lambda+q)(3\lambda+q+3) \quad (49)$$

We deduce similarly the following conditions in order that  $a_2$  and  $a_3$  may be finite

$$4\beta = (3\lambda+q)(3\lambda+q+3) \quad (50)$$

and 
$$0 = (3\lambda+q)(3\lambda+q+3) \quad (51)$$

It is easily seen that (49), (50) and (51) are simultaneously satisfied when  $\lambda=q=\beta=0$ . In that case we have from (47) that  $n'=0$ , or the period is infinite, which means that the star is in neutral equilibrium. This is also evident from the fact that when  $q=0$ , then  $\alpha=0$  and  $\gamma=4/3$ , from (4). We know that for stability,  $\gamma>4/3$ .

The model therefore cannot execute stable radial oscillations of large amplitude.

The author considers it a great privilege to record his sincere thanks to Professor A. C. Banerji, under whose guidance he has carried out the above investigation.

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA (SECTION A)

Part 4]

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## ON WARING'S PROBLEM (*mod p*)\*

BY INDER CHOWLA

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### SECTION 1 INTRODUCTION

Let  $p$  denote a prime. We suppose throughout that  $k$  is a positive integer. Let  $l$  be a positive integer and let  $\Gamma(k, p^l)$  be the least  $s$  such that every residue class (*mod p* <sup>$l$</sup> ) is representable as  $x_1^k + \dots + x_s^k$  where the  $x$ 's are integers and at least one of them is prime to  $p$ . After Hardy and Littlewood† the number  $\Gamma(k)$  is defined by

$$\Gamma(k) = \text{Max } \Gamma(k, p^l) \\ p \geq 2, l \geq 1$$

Hardy and Littlewood† have shown that  $\Gamma(k)$  is, when  $k=2$  and  $k \geq 4$ , the least  $s$  such that every arithmetical progression contains an infinity of numbers which are sums of at most  $s$  positive  $k$ th powers. If  $k=2$ , they‡ proved that

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\* This paper is the substance of a dissertation which was approved for the Ph.D. Degree of *Cambridge University* (1940).

† G. H. Hardy and J. E. Littlewood, "Some problems of 'Partitio Numerorum' (IV). The singular series in Waring's Problem and the value of the number  $G(k)$ ," *Math. Zeitschrift* 12 (1922), 161–188, and "Some problems of Partitio Numerorum (VIII). The number  $\Gamma(k)$  in Waring's Problem," *Proc. London Math. Soc.*, 28 (1928), 518–542. We shall refer to these memoirs as P. N. 4 and P. N. 8.

‡ P. N. 8, Theorem 1. This theorem is not true for  $k=1, 2, 4$  since  $\Gamma(1)=2$ ,  $\Gamma(2)=5$ ,  $\Gamma(4)=16$ .

§ P. N. 8, Theorem 4.

$4k$  is an upper bound for  $\Gamma(k)$ , while  $\Gamma(k) \leq k$  unless  $k$  belongs to one of the following special classes

- (i)  $k = 2^v$ ,  $v > 1$ ,  $\Gamma(k) = 2^{v+2} = 4k - k + 1$
- (ii)  $k = 2^v - 3$ ,  $v > 1$ ,  $\Gamma(k) = 2^{v+1} = 4 \frac{k}{3} > k + 1$
- (iii)  $k = p^v(p-1)$ ,  $p \geq 2$ ,  $v \geq 0$ ,  $\Gamma(k) = p^{v+1} > k + 1$
- (iv)  $k = \frac{1}{2}p^v(p-1)$ ,  $p \geq 2$ ,  $v \geq 0$ ,  $\Gamma(k) = \frac{1}{2}(p^{v+1}-1) > k + 1$  except in the particular case  $k = 3 = \frac{1}{2} \cdot 3(3-1)$  when  $\Gamma(k) = k + 1$
- (v)  $k = p-1$ ,  $p \geq 2$ ,  $k$  not belonging to any preceding class,  $\Gamma(k) = k + 1$
- (vi)  $k = \frac{1}{2}(p-1)$ ,  $p \geq 2$ ,  $k$  not belonging to any preceding class,  $\Gamma(k) = k$

We shall chiefly be concerned with the function  $\delta(k, p)$  which we define as the least  $s$  such that every residue class (mod  $p$ ) is representable as  $x_1^k + \dots + x_s^k$  where the  $x_i$ 's are integers. We note that  $\delta(k, p) \leq \Gamma(k, p) \leq \delta(k, p) + 1$ . Hardy and Littlewood\* proved that  $\Gamma(k, p) \leq (k, p-1)$  if  $p-1 \nmid k$ , while  $\Gamma(k, p) = p$  if  $p-1 \mid k$ , where  $(l, n) = 1$ ,  $p \geq 2$ . If  $p=2$  it is trivial that  $\Gamma(k, p) = \delta(k, p) + 1 = 2$ , since 0, 1 are the only  $k$ th power residues (mod  $p$ ).

Let  $p \geq 2$ . We write

$$\begin{aligned}(p-1, k) &= k_1 \\ p-1 &= k_1 t \\ k &= k_1 k_2\end{aligned}$$

Let  $g$  be a primitive root (mod  $p$ ). If  $(n, p)=1$  we have

$$\begin{aligned}n &\equiv g^b \pmod{p}, & 1 \leq b \leq p-1 \\ b k_1 + r(p-1) & & k_1(b+r t) \\ n^{k_1} &\equiv g & \equiv g\end{aligned}$$

for every integer  $r$ . Since  $(t, k_2)=1$ , a suitable choice of  $r$  gives

$$b + r t \equiv 0 \pmod{k_2}$$

Hence

$$\delta(k, p) = \delta((k, p-1), p)$$

We shall therefore investigate  $\delta((k, p), p)$  where  $p \equiv 1 \pmod{k}$ . Let  $p = tk + 1$ . If  $t=1$  or  $t=2$  it is trivial that  $\delta(k, p) = k$  since 0, 1 or 0, -1, +1 are the only  $k$ th power residues (mod  $p$ ). We shall prove that if  $p = tk + 1$ ,  $t \geq 2$  then for every  $\varepsilon > 0$ ,

$$\delta(k, p) = O(k^{t-C+\varepsilon}) \text{ where } C = \frac{103 - 3\sqrt{641}}{220}.$$

This result is equivalent to Theorem 3. We shall prove the following theorems

*Theorem 1* Let  $p = tk + 1$ ,  $t \geq 2$ . Then

$$\delta(k, p) = O(p^{\frac{1}{2}})$$

\* P. N. 8, Theorem 1 and Lemma 7

*Theorem 2* Let  $p = tl + 1 = l^{1+\rho}$ ,  $l \geq \sqrt[3]{3-1}$ ,  $\rho \leq \frac{3}{2}$ . Let  $\chi(k, p) = l^{1-\beta}$

Then  $\lim_{k \rightarrow \infty} \beta \geq \min \left( \frac{1}{3}, \frac{1}{\rho} + \frac{3}{8} - \frac{11}{8(4\rho+1)} \right)$  uniformly in  $p$

*Theorem 3* Let  $p = tl + 1$ ,  $l \geq 2$ . Let

$$(l, p) = l^{1-\beta}$$

Then  $\lim_{k \rightarrow \infty} \beta \geq \frac{103-3\sqrt{641}}{220}$  uniformly in  $p$

In addition we extend Theorem 3 to prove

*Theorem 4* Let  $p$  be an odd prime,  $l$  a positive integer and let  $C =$

$$\frac{103-3\sqrt{641}}{220}. \quad \text{Then for every positive } k$$

$$(A) \quad \Gamma(k, p^l) = O(k^{1-(1+\epsilon)/l}) \text{ if } p \geq 1 \text{ and } l \geq (p-1)^{1/k}.$$

$$(B) \quad \Gamma(k) = \max(M_1, M_2, M_3, M_4, M_5)$$

where

$$M_1 = O(k^{1-(1+\epsilon)/l}), \quad M_2 = \max_{l \geq 1} 2^{l+1}, \quad 2^l/l \geq 1$$

$$M_3 = \max_{l \geq 1} p^l, \quad M_4 = \max_{l \geq 1} \frac{1}{l} (p^l - 1), \quad M_5 = \max_{l \geq 1} \frac{1}{l} (3^l - 1)$$

$$\phi(p^l)^{1/k}, \quad \frac{1}{l} \phi(p^l)/k, \quad 3^{l-1}/k$$

$$p \geq 3, l \geq 1, \quad p \geq 5, l \geq 1, \quad l \geq 2$$

and a maximum is taken as **zero** if the conditions stated beneath it are not satisfied and  $\phi$  is Euler's function

Theorem 4 is proved by elementary methods. We use the following result due to Davenport\* on the addition of residue classes (*mod*  $p$ )

**LEMMA 1** Let  $p$  be a prime, let  $\alpha_1, \dots, \alpha_m$  be  $m$  different residue classes (*mod*  $p$ ), let  $\beta_1, \dots, \beta_n$  be  $n$  different residue classes (*mod*  $p$ ). Let  $\gamma_1, \dots, \gamma_l$  be all those different residue classes which are representable as

$$\alpha_i + \beta_j, \quad (1 \leq i \leq m, 1 \leq j \leq n).$$

Then  $l \geq m+n-1$  if  $m+n-1 \leq p$  and otherwise  $l \geq p$

The proof of Theorem 2 is based on different ideas and involves more complicated arguments. Let  $p = tl + 1$ ,  $l \geq 2$  and let  $u_1, \dots, u_t$  denote the  $t$  distinct  $k$ th power residues (*mod*  $p$ ) which are prime to  $p$ . We consider the exponential sums

$$S_{a,p} = \sum_{x=0}^{p-1} e^{\frac{2\pi i ax^k}{p}} = 1 + \frac{1}{l} \sum_{1 \leq r \leq l} e^{\frac{2\pi i ar}{p}} \quad (1 \leq a < p)$$

\* *Journ of London Math Soc*, 10 (1935) 30-32



Let  $M(p, n, s)$  denote the number of resolutions of  $n$

$$h_1^k + \dots + h_s^k \equiv n \pmod{p} \quad 0 \leq h_i < p$$

We have the identity,

$$\frac{M(p, n, s)}{p^s - 1} = 1 + p^{-1} \sum_{1 \leq a < p} (S_{a,p})^s e^{\frac{2\pi i a n}{p}}$$

$$\text{If } \left| p^{-1} \sum_{1 \leq a < p} (S_{a,p})^s \right| < 1 \text{ then } M(p, n, s) > 0 \text{ and } \chi(k, p) \leq s$$

Let  $p = k^{1+\epsilon}$ . We have\*

$$|S_{a,p}| \leq (k-1)\sqrt{p} \quad (1 \leq a < p)$$

Thus if  $p > C_1 > 1$  where  $C_1$  is an absolute constant, it is easy to show that

$$\chi(k, p) = O(1)$$

If the modulus of each of the exponential sums for  $1 \leq a < p$  was sufficiently small, we could use the classical argument in the proof of Theorem 2, to obtain a non-trivial upper bound for  $\chi(k, p)$ . If, on the other hand, for at least one integer  $a_0$  with  $1 \leq a_0 < p$ ,  $|S_{a_0, p}|$  is sufficiently close to  $p$ , we may expect some regularity in the distribution of the numbers  $a_0 u_1, \dots, a_0 u_r$  in the interval  $(0, p)$ . We make use of this idea in developing the main arguments of the proof

Theorems 1 and 2 and

$$\chi(k, p) = O(1) \quad (p \geq k^2)$$

give Theorem 3

I wish to record my deep gratitude to Dr Heilbronn for his guidance throughout the preparation of this paper

## SECTION 2 NOTATION

Throughout  $k$  is a positive integer

$$C = \frac{103 - 3\sqrt{641}}{220}$$

$p$  will denote a prime

$$S_{a,p} = \sum_{r=0}^{p-1} e^{\frac{2\pi i a r^k}{p}}$$

where  $a$  is an integer with  $1 \leq a < p$

\* See Landau, *Vorlesungen über Zahlentheorie*, Bd 1, Satz 811

Let  $M(p, n, s)$  denote the number of solutions of  $h_1^k + \dots + h_s^k \equiv n \pmod{p}$ ,  $0 \leq h_i < p$

$\phi$  is Euler's function

We use the symbol  $|x|$  to denote the greatest integer not exceeding  $x$

In sections 3, 4, 5 and 6

$$p = tk + 1, t \geq 2$$

We shall use  $u$  to denote a  $k$ th power residue  $\pmod{p}$  which is prime to  $p$  and  $u_1, \dots, u_t$  will denote the  $t$  distinct  $k$ th power residues  $\pmod{p}$  which are prime to  $p$ . We have

$$S_{a, p} = \sum_{x=0}^{p-1} e^{\frac{2\pi i ax^k}{p}} = 1 + k \sum_{1 \leq r \leq t} e^{\frac{2\pi i au_r}{p}} = 1 + \sum_u e^{\frac{2\pi i au}{p}},$$

We use the following notation in section 7

Let  $l$  be a positive integer. We shall denote by  $\Delta(k, p^l, n)$  the least number  $s$  such that the residue class  $n \pmod{p^l}$  is representable as  $\pm x_1^k \pm \dots \pm x_s^k$  where the  $x$ 's are integers and at least one of them is prime to  $p$ . Then  $\Delta(k, p^l)$  is defined by

$$\Delta(k, p^l) = \text{Max } \Delta(k, p^l, n) \\ 0 \leq n < p$$

We define  $\Gamma(k, p^l, n)$  as the least number  $s$  such that the residue class  $n \pmod{p^l}$  is representable as  $x_1^k + \dots + x_s^k$  where the  $x$ 's are integers and at least one of them is prime to  $p$ . Hence

$$\Gamma(k, p^l) = \text{Max } \Gamma(k, p^l, n) \\ 0 \leq n < p$$

### SECTION 3. PROOF OF THEOREM 1

We have  $p = tk + 1$ ,  $t \geq 2$ . Since  $t \geq 2$  we can find a  $k$ th power residue  $R \not\equiv \pm 1 \pmod{p}$  which is prime to  $p$ . We consider the least positive residue  $\pmod{p}$  of  $hR$  for  $1 \leq h \leq [p^{\frac{1}{k}}]$ . Then the numbers

$$0, R, \dots, [p^{\frac{1}{k}}]R, p$$

define  $[p^{\frac{1}{k}}] + 2$  different points distributed among the  $[p^{\frac{1}{k}}] + 1$  intervals

$$r p^{\frac{1}{k}} \leq \xi < (r+1)p^{\frac{1}{k}} \quad (r = 0, 1, \dots, [p^{\frac{1}{k}}])$$

At least one interval must contain two points, hence we can find  $x, y$  such that

$$R \equiv xy^{-1} \pmod{p}$$

where

$$1 \leq y < p^{\frac{1}{k}}, \quad |x| < p^{\frac{1}{k}}$$

We may assume without loss of generality that  $(x, y) = 1$ , and that  $|x| > y$  since otherwise we can substitute  $R^{-1}$  for  $R$  in the argument. Hence

$$R \equiv xy^{-1} \pmod{p}$$

where  $|x| \leq y < |x| < p^{\frac{1}{2}} \quad (x, y) = 1$

We consider the following cases

Case I  $p' \nmid |x| < p^{\frac{1}{2}}$

It is easily proved that the members

$$(1) \quad m + nR \quad \left( 0 \leq m, n < \frac{p^{\frac{1}{2}}}{2} \right)$$

are mutually incongruent  $\pmod{p}$ . For if any two of these numbers, say,  $m_1 + n_1 R, m_2 + n_2 R$  were congruent  $\pmod{p}$ , we should have

$$R \equiv xy^{-1} \equiv (m_1 - m_2)(n_1 - n_2)^{-1}$$

$$x(n_2 - n_1) - y(m_1 - m_2) \equiv 0$$

Since  $|x(n_2 - n_1) - y(m_1 - m_2)| < p^{\frac{1}{2}} \cdot p^{\frac{1}{2}} < p$  it follows that

$$x(n_2 - n_1) = y(m_1 - m_2)$$

Since  $(x, y) = 1$  we have  $x \mid m_1 - m_2$ . But  $|x| < p^{\frac{1}{2}} < |m_1 - m_2|$

Hence  $m_1 = m_2$ , and consequently  $n_1 = n_2$ .

Hence the set (1) consists of  $\left( \left\lfloor \frac{p^{\frac{1}{2}}}{2} \right\rfloor + 1 \right)^2 \cdot \frac{p^{\frac{1}{2}}}{4}$  mutually incongruent numbers  $\pmod{p}$  which are sums of at most  $p^{\frac{1}{2}}$   $k$ th power residues  $\pmod{p}$ . Repeated application of Lemma 1 to the set (1) gives

$$\varepsilon(k, p) \leq p^{\frac{1}{2}} \left( \left( \left\lfloor \frac{p^{\frac{1}{2}}}{2} \right\rfloor + 1 \right)^2 + 1 \right) = O(p^{\frac{1}{2}})$$

Case II  $|x| < p^{\frac{1}{2}}$

We observe that  $|x| > y \geq |x|$ . We can find a positive integer  $f$  such that

$$\frac{p^{\frac{1}{2}}}{p^{\frac{1}{2}}} = p^{\frac{1}{2}} < |x|^f < p^{\frac{1}{2}}$$

We have

$$R^f \equiv x^f y^{-f} \pmod{p}$$

where  $(x^f, y^f) = 1$ ,  $1 \leq y^f < |x|^f < p^{\frac{1}{2}}$ ,  $|x|^f > p^{\frac{1}{2}}$  and  $R^f$  is a  $k$ th power residue  $\not\equiv \pm 1 \pmod{p}$ .

Consider the numbers

$$(2) \quad m + nR^f \quad \left( 0 \leq m, n < \frac{p^{\frac{1}{2}}}{2} \right)$$

If any two of these numbers say,  $m_1 + n_1 R^f$ ,  $m_2 + n_2 R^f$  were congruent (mod  $p$ ), we should have

$$R^f \equiv x^f y^{-f} \equiv (m_1 - n_1)(n_2 - n_1)^{-1}$$

$$x^f(n_2 - n_1) - y^f(m_1 - m_2) \equiv 0$$

Now  $|x^f(n_2 - n_1) - y^f(m_1 - m_2)| < p^{\frac{1}{2}} p^{\frac{1}{2}} = p$ , hence

$$x^f(n_2 - n_1) = y^f(m_1 - m_2)$$

Since  $(x^f, y^f) = 1$ , it follows that  $x^f/m_1 - m_2$ . But  $|x|^f < p^{\frac{1}{2}} < |m_1 - m_2|$

Hence  $m_2 = m_1$ , therefore  $n_1 = n_2$ .

Thus (2) comprises  $\left( \left[ \frac{p^{\frac{1}{2}}}{2} \right] + 1 \right)^2 > \frac{p^{\frac{1}{2}}}{4}$  mutually incongruent num-

bers (mod  $p$ ) which are sums of at most  $p^{\frac{1}{2}}$   $k$ th power residues (mod  $p$ ). Repeated application of Lemma 1 to the set (2) gives

$$\delta(k, p) \leq p^{\frac{1}{2}} \left( \left| \left( \left[ \frac{p^{\frac{1}{2}}}{2} \right] + 1 \right)^2 - 1 \right| + 1 \right) = O(p^{\frac{1}{2}})$$

Case III.

$$p^{\frac{1}{2}} < |x| < p.$$

We consider the numbers

$$(3) \quad l + mR + nR^2 \quad (0 \leq l, m, n < \frac{1}{2}p^{\frac{1}{2}})$$

If any two of these numbers, say,  $l_1 + m_1 R + n_1 R^2$ ,  $l_2 + m_2 R + n_2 R^2$  were congruent (mod  $p$ ), we should have

$$(l_1 - l_2) + (m_1 - m_2)R + (n_1 - n_2)R^2 \equiv 0 \pmod{p}.$$

$$(l_1 - l_2) + (m_1 - m_2)xy^{-1} + (n_1 - n_2)x^2y^{-2} \equiv 0 \pmod{p},$$

$$(l_1 - l_2)y^2 + (m_1 - m_2)xy + (n_1 - n_2)x^2 \equiv 0 \pmod{p}$$

Since  $|(l_1 - l_2)y^2 + (m_1 - m_2)xy + (n_1 - n_2)x^2| < \frac{3}{2}p^{\frac{1}{2}}p^{\frac{1}{2}} = p$ , it follows that

$$(l_1 - l_2)y^2 + (m_1 - m_2)xy + (n_1 - n_2)x^2 = 0$$

Since  $(x, y) = 1$ , we have  $x \mid l_1 - l_2$ . But  $|x| > p^{\frac{1}{2}} > |l_1 - l_2|$

Hence  $l_1 = l_2$ , and since  $x \neq 0$ ,  $y(m_1 - m_2) + x(n_1 - n_2) = 0$

Hence  $x/m_1 - m_2$ , since  $(x, y) = 1$ . Since  $|x| > p^{\frac{1}{2}} > |m_1 - m_2|$  it follows that  $m_1 = m_2$ , consequently  $n_1 = n_2$ .

Thus (3) consists of  $\left( \left[ \frac{p^{\frac{1}{k}}}{3} \right] + 1 \right)^3 > \frac{p^{\frac{1}{k}}}{27}$  mutually incongruent numbers which are sums of at most  $p^{\frac{1}{k}}$   $k$ th power residues ( $\text{mod } p$ ). Repeated application of Lemma 1 to the set (3) gives

$$\gamma(k, p) \leq p^{\frac{1}{k}} \left( \left[ \left( \left[ \frac{p^{\frac{1}{k}}}{3} \right] + 1 \right)^3 - 1 \right] + 1 \right) = O(p^{\frac{1}{k}})$$

This completes the proof of Theorem 1

#### SECTION 4. LEMMAS FOR THE PROOF OF THEOREM 2

LEMMA 2 (i) Let  $d = |u_i - u_j| > 1$ , where  $i \leq t, j \leq t$ . Then

$$\gamma(k, p) \leq 2d^{\frac{\log p}{\log d}}$$

(ii) Let  $d = \sum_{r=1}^s u_r, s \geq 2$ . Then

$$\gamma(k, p) \leq 2d^{\frac{\log p}{\log d}}$$

Proof of (i) Let  $h = \left[ \frac{\log p}{\log d} \right]$ , then every integer  $n$  with  $0 \leq n \leq p$  is expressible as

$$\begin{aligned} n &= \sum_{\mu=0}^h x_{\mu} d^{\mu} \quad (0 \leq x_{\mu} \leq d-1) \\ &= \sum_{\mu=0}^h x_{\mu} \sum_{\nu=0}^{\mu} (-1)^{\nu} \binom{\mu}{\nu} u_i^{\mu-\nu} u_j^{\nu} \\ &= - \sum_{\mu=0}^h (d-1) \sum_{\substack{\nu=1 \\ \nu \equiv 1(2)}}^{\mu} \binom{\mu}{\nu} u_i^{\mu-\nu} u_j^{\nu} + \sum_{\mu=0}^h (d-1-x_{\mu}) \sum_{\substack{\nu=1 \\ \nu \equiv 1(2)}}^{\mu} \binom{\mu}{\nu} u_i^{\mu-\nu} u_j^{\nu} \\ &\quad + \sum_{\mu=0}^h x_{\mu} \sum_{\substack{\nu=0 \\ \nu \equiv 0(2)}}^{\mu} \binom{\mu}{\nu} u_i^{\mu-\nu} u_j^{\nu} \end{aligned}$$

\* In other words,  $d$  is congruent ( $\text{mod } p$ ) to the difference of two  $k$ th powers.

† Here  $d$  is congruent ( $\text{mod } p$ ) to the sum of  $s$   $k$ th powers

We observe now that the first sum is a fixed residue class  $(\text{mod } p)$ , every term is positive in the remaining sums. Therefore  $n$  is representable as  $h_1^{s_1} + h_2^{s_2}$  where  $m \leq (d-1)(2^{d+1}-1) < d2^{d+1}f/\log d$  which proves (i).

Proof of (ii). Let  $h = \begin{Bmatrix} \log p \\ \log d \end{Bmatrix}$  if  $0 \leq n \leq p$  we can express  $n$  in the form

$$n = \sum_{\mu=0}^h c_\mu d^\mu \quad (0 \leq c_\mu \leq d-1)$$

Since  $d$  is a sum of  $s$   $k$ th power residues  $(\text{mod } p)$   $n$  is a sum of at most

$$(d+1) \sum_{\mu=0}^h c_\mu \leq (d+1) \sum_{\mu=0}^h \frac{(s^{d+1}-1)}{s^{d+1}-1} c_\mu \leq d^{\log_e \log_e p} d^{\log_e \log_e d} k \text{th power residue } (\text{mod } p) \quad \text{This proves (ii)}$$

LEMMA 2\*. Let  $h$  be a positive integer, let  $\alpha_1, \dots, \alpha_m$  be  $m$  different residue classes  $(\text{mod } h)$ , let  $\beta_1, \dots, \beta_n$  be  $n$  different residue classes  $(\text{mod } h)$  where one of the  $\beta$ 's is zero and the rest are prime to  $h$ . Let  $\gamma_1, \dots, \gamma_l$  be all those different residue classes which are representable as

$$\alpha_i + \beta_j \quad (1 \leq i \leq m, 1 \leq j \leq n)$$

Then  $l \geq m+n-1$  if  $m+n-1 \leq h$  and otherwise  $l=h$ .

LEMMA 1. Let  $H$  be a positive integer, let  $b_1, \dots, b_T$  be  $T$  different residue classes  $(\text{mod } H)$ . Then

$$(4) \quad \sum_{1 \leq j \leq s} b_j \equiv O(\text{mod } H)$$

is soluble with

$$s = O\left(\frac{H \log \log H}{T}\right)$$

Proof. Let  $N(H, T)$  denote the least  $s$  such that (4) is soluble, let  $G(H, T)$  denote the least  $s$  such that (4) is soluble under the assumption that all the given  $b$ 's are prime to  $H$ . Then Lemma 3 asserts that

$$(5) \quad G(H, T) \leq \left\lfloor \frac{H}{T} \right\rfloor + 1 \leq \frac{2H}{T}$$

\* This is a generalisation of Lemma 1, with certain restrictions on one of the sequences. See I. Chowla, "A theorem on the addition of residue classes: application to the number  $F(k)$  in Waring's problem," *Quart. J. Math. (Oxford)*, 8(1937), 99-102. See also, *Cambridge Tracts in Mathematics and Mathematical Physics*, No. 35 (by F. Landau), Kapitel 4.

Let  $d$  ( $1 \leq i \leq d(H)$ ) run over the divisors of  $H$  where  $i(H)$  denotes the number of divisors of  $H$ , let  $t$  be the number of  $b$ 's for which  $(b, H) = d$  ( $1 \leq i \leq d(H)$ ). We have from (5)

$$(6) \quad i(H, 1) \leq G \left( \frac{H}{d} \right)^t \leq \frac{2H}{d^t} \text{ for } 1 \leq i \leq i(H)$$

also

$$(7) \quad \sum_{1 \leq i \leq d(H)} t_i = T$$

It is a well known result\* that  $\sigma(H) < C_1 H \log^{-1} H$  where  $\sigma(H)$  is the sum of the divisors of  $H$  and  $C_1$  is an absolute constant. Hence

$$(8) \quad \sum_{1 \leq i \leq d(H)} \frac{1}{d} = \frac{1}{H} \sigma(H) < c_2 \frac{H \log \log H}{H} = c_2 \log \log H$$

If  $1/t < c_2 \log \log H$  for every  $i$  with  $1 \leq i \leq i(H)$

we should have, applying (7) and (8)

$$1 = \sum_{1 \leq i \leq d(H)} t < c_2 \log \log H \sum_{1 \leq i \leq d(H)} \frac{1}{d} < 1$$

which is impossible. Hence there exists an  $i$  with

$$1 \leq i \leq i(H) \text{ such that } 1/t \geq \frac{1}{c_2 \log \log H} \text{ where } c_2 \text{ is an absolute}$$

constant. We have from (6)

$$i(H, 1) \leq \frac{2H}{d^t} \leq \frac{2c_2 H \log \log H}{T} = O \left( \frac{H \log \log H}{1} \right)$$

which proves the lemma.

LEMMA 5

Let  $0 < \delta < 1$ , let

$$\left| \sum_n e^{\frac{2\pi i a n}{p}} \right| \leq t \left( 1 - \frac{3 \log p}{p^{1-\delta}} \right)$$

for every  $a$  with  $1 \leq a < p$ . Then

$$8(t/p) < p^{1-\delta}$$

Proof. We have

$$\left| S_{a/p} \right| = 1 + \sum_n e^{\frac{2\pi i a n}{p}} \leq 1 + (p-1) \left( 1 - \frac{3 \log p}{p^{1-\delta}} \right) < p \left( 1 - \frac{2 \log p}{p^{1-\delta}} \right)$$

\* See Hardy and Wright 'An Introduction to the Theory of Numbers' Theorem 323

since  $p > 3$ . We have the identity

$$\frac{M(p, n, s)}{p^{s-1}} = 1 + p^{-s} \sum_{1 \leq a < p} \left( \frac{a}{p} \right)^s e^{-2\pi i a n / p}$$

Put  $s = \left\lfloor \frac{k^{1-\delta}}{2} \right\rfloor + 1$ . Then  $M(p, n, s) \sim 0$

$$\begin{aligned} \text{since} \quad & \left| p^{-s} \sum_{1 \leq a < p} \left( \frac{a}{p} \right)^s e^{-\frac{2\pi i a n}{p}} \right| < p^{-s} p^{-s'} \left( 1 - \frac{2}{k^{1-\delta}} \right)^s \\ & = p \left( 1 - \frac{2 \log p}{k^{1-\delta}} \right)^{\left\lfloor \frac{k^{1-\delta}}{2} \right\rfloor + 1} p \left( 1 - \frac{2 \log p}{k^{1-\delta}} \right)^{\frac{1}{2} k^{1-\delta} - \log p} \leq p e^{-\log p} = 1 \end{aligned}$$

Hence the lemma

LEMMA 6. Let  $a_0$  be an integer with  $1 \leq a_0 < p$  such that

$$(4) \quad \left| \sum_u e^{\frac{2\pi i a_0 u}{p}} \right| \leq t \left( 1 - \frac{3 \log p}{k^{1-\eta}} \right), \quad 0 < \eta < 1, \quad \text{and let } \lambda > 0 \text{ be defined}$$

by the equation

$$X^2 = \frac{3p^2 \log p}{\pi^\lambda k^{1-\eta}}, \quad 0 < \lambda < 1$$

Let  $a_0 u$  denote the residue (mod  $p$ ) of  $a_0 u$  in the interval  $(-\frac{1}{2}p, \frac{1}{2}p)$ . Then there exists a real number  $\sigma$  such that  $|a_0 u - p\sigma|$  differs from 0 on  $p$  by less than  $X$  for at least  $t(1-\lambda)$  values of  $u$ .

Proof. A suitable choice of  $\sigma$  with  $-\frac{1}{2} \leq \sigma < \frac{1}{2}$  gives

$$0 < \sum_u e^{\frac{2\pi i}{p} \left( \frac{a_0 u}{p} - \sigma \right)} = \sum_u \cos 2\pi \left( \frac{a_0 u}{p} - \sigma \right)$$

We have from (4)

$$t > \sum_u \cos 2\pi \left( \frac{a_0 u}{p} - \sigma \right) > t \left( 1 - \frac{3 \log p}{k^{1-\eta}} \right)$$

$$(10) \quad 0 < \sum_u \left( 1 - \cos 2\pi \left( \frac{a_0 u}{p} - \sigma \right) \right) \leq \frac{3t \log p}{k^{1-\eta}}$$

Suppose

$$(11) \quad \lambda \leq |a_0 u - p\sigma| \leq p - \lambda,$$

then

$$\begin{aligned} 1 - \cos 2\pi \left( \frac{a_0 u}{p} - \sigma \right) &= 1 - \cos \frac{2\pi}{p} |a_0 u - p\sigma| \geq 1 - \cos \frac{2\pi X}{p} \\ &\geq 1 - \left( 1 - \frac{\pi^2 X^2}{p^2} \right) = \frac{\pi^2 X^2}{p^2} \end{aligned}$$

$$\text{since} \quad \cos \psi \leq 1 - \frac{\psi^2}{A} \quad (0 \leq \psi \leq \pi)$$



If (11) holds for  $m$  values of  $n$ , we have from (10):

$$\frac{m\pi^2 X^2}{p^2} = \frac{3m \log p}{\lambda k^{1-\eta}} < \frac{3t \log p}{k^{1-\eta}},$$

$$\frac{m}{\lambda} < t, m < t\lambda$$

or,

$$t - m > t(1 - \lambda)$$

which proves the lemma.

LEMMA 7. Let  $t$  be sufficiently large and let for at least one integer  $a_0$  ( $1 \leq a_0 < p$ )

$$\left| \sum_n e^{2\pi i a_0 n} \right| < t \left( 1 - \frac{3 \log p}{\lambda k^{1-\eta}} \right), \quad 0 < \eta < 1$$

Let  $Z = \exp \left( \frac{8 \log p}{\log \log p} \right)$ . Then there is a positive  $Y \leq X$  (where  $X$  is defined in Lemma 6 with  $\lambda = (\log p)^{-1}$ ) and a positive integer  $a \leq \frac{Y Z}{t}$  such that there are at least  $\frac{t}{2 \log^2 p}$  of the numbers  $an$  which satisfy  $Y \leq |an| \leq 2Y$ .

Proof. We write  $n = [t \log \log p] + 1$ ,  $k$  is taken sufficiently large in order that  $2^{t+1} \leq t \log p$ . By Lemma 6\* at least  $t(1-\lambda)$  of the numbers  $a_0 n$  are contained in the interval  $(p\sigma - X, p\sigma + X)$  where  $\sigma$  is a real number. We divide this interval which contains at least  $[t(1-\lambda)] + 1$  of the numbers  $a_0 n$  into  $[t(1-\lambda)]$  sub-intervals each of length  $= \frac{2X}{[t(1-\lambda)]}$ . Applying the argument that if there are  $f+1$  points distributed among  $f$  intervals, at least one of the  $f$  intervals must contain two points, we can find  $u_i, u_j$  ( $1 \leq i, j \leq t, i \neq j$ ) such that  $0 < a_0(u_i - u_j) \leq \frac{2X}{[t(1-\lambda)]} < \frac{2X}{t(1-\lambda) - 1}$ . We define  $Y_0 = \frac{1}{2}X$ ,  $a_1 = a_0(u_i - u_j)$ .

At least  $t(1-\lambda)$  of the numbers  $a_0 u_i$  as well as of the numbers  $a_0 u_j$  are contained in the same interval  $(p\sigma - 2Y_0, p\sigma + 2Y_0)$ , hence there are at least  $t(1-2\lambda)$  of the numbers  $a_0 u_i(u_i - u_j) = a_1 u_i$  contained in  $(-4Y_0, 4Y_0)$ . We divide the interval  $(-4Y_0, 0)$  into sub-intervals of the type  $\left(-\frac{1}{2^m}Y_0, -\frac{1}{2^{m+1}}Y_0\right)$  and the interval  $(0, 4Y_0)$  into sub-intervals of the type  $\left(\frac{1}{2^{m+1}}Y_0, \frac{1}{2^m}Y_0\right)$  where  $-2 \leq m < \log p$ . Now we choose the smallest integer  $m$  with  $-2 \leq m < \log p$  such that if  $Y_1 = \frac{1}{2^{m+1}}Y_0$

\* Lemma 6 asserts that  $a_0 u - p\sigma$  differs from 0 or  $p$  by less than  $X$  for at least  $t(1-\lambda)$  values of  $u$ . We take the residue  $(\text{mod } p)$  of  $\{a_0 u - p\sigma\}$  which lies in the interval  $(-\frac{1}{2}, \frac{1}{2}p)$ . Then  $|a_0 u - p\sigma| \leq X$  or  $p\sigma - X \leq a_0 u \leq p\sigma + X$  for at least  $t(1-\lambda)$  values of  $u$ .

there are at least  $\frac{t(1-2\lambda)}{\log^2 p}$  of the numbers  $a_1 u$  which satisfy  $Y_1 \leq |a_1 u| \leq 2Y_1$ ; this is possible since there are at least  $t(1-2\lambda)$  of the numbers  $a_1 u$  and not more than  $2 \log p + 6$  intervals. It is evident from our choice of  $Y_1$  that there are not more than  $\frac{t(1-2\lambda)}{\log^2 p} (\log p + 2)$  of the numbers  $a_1 u$  which satisfy  $2Y_1 \leq |a_1 u| \leq 4Y_1$ . There are at least  $t(1-2\lambda)$  of the numbers  $a_1 u$  in  $(-4Y_1, 4Y_1)$  and therefore there are at least  $t(1-2\lambda) - \frac{t(1-2\lambda)}{\log^2 p} (\log p + 2) \geq t(1-2^2\lambda)$  of the numbers  $a_1 u$  in  $(-2Y_1, 2Y_1)$ .

If  $Y_1 \geq 8Y_0 Z^{-1}$ , we have  $a_1 \leq \frac{4Y_0}{t(1-\lambda)-1} < \frac{8Y_0}{t} \leq \frac{Y_1 Z}{t}$ ,  $Y_1 \leq 2Y_0 = X$ , and since there are at least  $\frac{t(1-2\lambda)}{\log^2 p} > \frac{t}{2 \log^2 p}$  of the numbers  $a_1 u$  which satisfy  $Y_1 \leq |a_1 u| \leq 2Y_1$ , the lemma would follow with  $Y = Y_1$ ,  $a = a_1$ .

Let  $Y_1 < 8Y_0 Z^{-1}$ . For the rest of the proof we depend on induction. If  $Y_{r-1} < 8Y_0 Z^{-1}$  for an  $r$  with  $2 \leq r \leq n$  and if there are at least  $t(1-2^{2r-2}\lambda)$  of the numbers  $a_{r-1} u$  in the interval  $(-2Y_{r-1}, 2Y_{r-1})$ , we define  $a_r$  and  $Y_r$  as follows. We define  $a_r = a_{r-1}(u_i - u_j)$  where  $u_i, u_j$  ( $1 \leq i, j \leq t$ ,  $i \neq j$ ) are chosen in such a way that  $0 < a_r \leq \frac{4Y_{r-1}}{t(1-2^{2r-2}\lambda)-1}$  and this is possible since there are at least  $t(1-2^{2r-2}\lambda)$  of the numbers  $a_{r-1} u$  contained in an interval of length  $\leq 4Y_{r-1}$ .

At least  $t(1-2^{2r-2}\lambda)$  of the numbers  $a_{r-1} u_i u_j$  as well as of the numbers  $a_{r-1} u_j u_i$  are contained in  $(-2Y_{r-1}, 2Y_{r-1})$ , hence there are at least  $t(1-2^{2r-1}\lambda)$  of the numbers  $a_{r-1}(u_i - u_j)u = a_r u$  in  $(-4Y_{r-1}, 4Y_{r-1})$ .  $Y_r$  is now defined in the following manner. We write  $Y_r = \frac{1}{2^{m+1}} Y_{r-1}$  where  $m$  is the smallest integer with  $-2 \leq m < \log p$  such that there are at least  $\frac{t(1-2^{2r-1}\lambda)}{\log^2 p}$  of the numbers  $a_r u$  which satisfy  $Y_r \leq |a_r u| \leq 2Y_r$ . It is not difficult to see that there are at least  $t(1-2^{2r-1}\lambda) - \frac{t(1-2^{2r-1}\lambda)}{\log^2 p} (\log p + 2) \geq t(1-2^{2r}\lambda)$  of the numbers  $a_r u$  contained in the interval  $(-2Y_r, 2Y_r)$ .

If for some  $r$ ,  $Y_r \geq 8Y_0 Z^{-1}$  the lemma is proved with  $Y = Y_r$ ,  $a = a_r$ . For we have at least  $\frac{t(1-2^{2r-1}\lambda)}{\log^2 p} > \frac{t}{2 \log^2 p}$  of the numbers  $a_r u$  which satisfy  $Y_r \leq |a_r u| \leq 2Y_r$ , where  $a_r \leq \frac{4Y_{r-1}}{t(1-2^{2r-2}\lambda)-1} \leq \frac{8Y_{r-1}}{t} \leq \frac{Y_r Z}{t}$  and  $Y_r \leq 2Y_{r-1} < 2 \cdot 2^{2^{r-1}-1} \cdot 2^{2^{r-1}-1} \cdot Y_0 = 2^{2^r-1} \cdot Z^{-1} \cdot X \leq X$ .

Otherwise we extend the induction to the case  $r=n$  and obtain a contradiction. For we have  $Y_n < 8Y_{n-1}x^{-1}$  where  $Y_n$  is such that there are at least  $t(1-2^{s_n}\lambda)$  of the numbers  $a_n u$  in  $(-2Y_n, 2Y_n)$ . In other words, we have at least  $t(1-2^{s_n}\lambda) \geq \frac{t}{2}$  of the numbers  $a_n u$  contained in an interval of length  $\leq 4Y_n < 4 \cdot 2^{s_n} x^{-1} Y_0 = 2^{s_n+1} x^{-1} X$ . But that is impossible because

$$\frac{t}{2} > 2^{s_n+1} x^{-1} X$$

since

$$x^n > p^2 > k^{\frac{1+\eta}{2}} \log^4 p > 2^{s_n+2} k^{\frac{1+\eta}{2}} \log p > 2^{s_n+2} k^{\frac{1+\eta}{2}} \cdot \frac{p}{p-1}.$$

$$\frac{\sqrt{8}}{\pi} \log p = 2^{s_n+1} \frac{X}{t}.$$

The assumption that we cannot find an  $r$  with  $1 \leq r \leq n$  such that  $Y_r \geq 8Y_{r-1}x^{-1}$  leads to a contradiction. Hence the lemma

## SECTION 5. PROOF OF THEOREM 2

We write,

$$\begin{aligned} b(l, p) &= l^{1-\beta}, \quad 0 < \beta < 1 \\ p &= tl + 1 = l^{1+\rho} \quad t > 2, \rho \leq 1 \end{aligned}$$

We put,

$$\omega = [\sqrt{\log l}]$$

Defining  $X$  (of Lemma 6) with  $\eta = \beta$ ,  $\lambda = (\log p)^{-1}$ , we have

$$X = O(p \cdot l^{-\frac{1-\beta}{2}} \log p)$$

If  $\left| \sum_{u=1}^{2\omega \log p} e^{\frac{2\pi i a u}{p}} \right| \leq t \left( 1 - \frac{3 \log p}{l^{1-\beta}} \right)$  for every  $a$  with  $1 \leq a < p$  then a contradiction

would follow from Lemma 5 with  $\beta = \beta$

We assume therefore that there exists at least one integer  $a_0$  ( $1 \leq a_0 < p$ ) such that

$$\left| \sum_{u=1}^{2\omega \log p} \frac{e^{2\pi i a_0 u}}{p} \right| > t \left( 1 - \frac{3 \log p}{l^{1-\beta}} \right)$$

Hence by Lemma 6 (with  $\eta=\beta$ ,  $\lambda=(\log p)^{-1}$ ) and Lemma 7 (with  $\eta=\beta$ ) we can find a positive  $Y \leq X$  and a positive integer  $a \leq \frac{Y \rho^{\frac{8}{\log \log p}}}{t}$  such that there are at least  $\frac{t}{2 \log^3 p}$  of the numbers  $au$  which satisfy  $Y \leq |au| \leq 2Y$

Without loss of generality it may be assumed that there are at least  $\frac{t}{4 \log^3 p}$  of the numbers  $au$  in the interval  $(Y, 2Y)$ . Let  $t_1$  be the number of  $au$ 's in  $(Y, 2Y)$ . Then

$$(12) \quad t_1 \geq \frac{t}{4 \log^3 p}$$

Suppose we have a residue class (mod  $a$ ) which contains  $r+1 \geq \omega+1$  numbers  $au_1, \dots, au_{r+1}$  satisfying

$$Y \leq au_1 < au_2 < \dots < au_{r+1} \leq 2Y$$

We consider the positive integers

$$\frac{au_{\omega+1} - au_1}{a}, \dots, \frac{au_{\left[\frac{r}{\omega}\right] + 1} - au_{\left(\left[\frac{r}{\omega}\right] - 1\right)\omega + 1}}{a}$$

Then number is  $\left[\frac{r}{\omega}\right]$ , each of them  $\geq \omega$  and their sum  $\leq \frac{Y}{a}$ . The smallest of them, say  $d$ , therefore satisfies

$$\omega \leq d \leq \frac{Y}{a \left[\frac{r}{\omega}\right]} < \frac{2Y\omega}{ar}$$

Now  $d$  is a difference of two  $k$ th power residues (mod  $p$ ), hence by Lemma 2(\*).

$$(13) \quad \begin{aligned} \chi(k, p) &\leq 2d 2^{\frac{\log p}{\log d}} \leq 2^2 Y_\omega (ar)^{-1} p^{\frac{\log 2}{\log \omega}} \\ &= O(X\omega(ar)^{-1} k^{\frac{\log 8}{\log \omega}}) = O(k^{\frac{1-\beta}{2} + \frac{\log 8}{\log \omega}}) \quad (ar) \omega p \log p \end{aligned}$$

We consider two cases :

$$I. \quad a \leq \frac{t}{4(\omega+1) \log^3 p}$$

Then by (12),

$$a \leq \frac{t_1}{\omega+1}, \frac{t_1}{a} \geq \omega+1.$$

Hence we can find a residue class (*mod*  $a$ ) which contains at least  $\frac{t_1}{a} \geq \omega + 1$  of the numbers  $au$ , or

$$, \geq \frac{t_1}{a} - 1 \geq \frac{t_1}{a}$$

Applying (12) and (13)

$$\delta(l, p) = O(l^{-\frac{1-\beta}{2} + \frac{\log 8}{\log \omega}} l^{-\omega \log^3 p}),$$

$$l^{1-\beta} = O(l^{\frac{1+\beta}{2} + \frac{\log 8}{\log \omega}} \omega \log^3 p),$$

$$1-\beta \leq \frac{1+\beta}{2} + O\left(\frac{1}{\log \omega}\right) + O\left(\frac{\log \omega}{\log l}\right) + O(1),$$

or

$$(14) \quad \beta \geq \frac{1}{2} + O\left(\frac{1}{\log \omega}\right) + O\left(\frac{\log \omega}{\log l}\right) + O(1)$$

II

$$a > \frac{t}{4(\omega+1) \log^2 p}$$

We first suppose that one residue class (*mod*  $a$ ) contains at least  $\omega + 1$  of the numbers  $au$ . Then  $d$  the difference between the smallest and the largest of them, divided by  $a$ , satisfies

$$\omega \leq d \leq \frac{Y}{a}$$

Since  $d$  is a difference of two  $k$ th power residues (*mod*  $p$ ), we have applying Lemma 2(s) :

$$\begin{aligned} \delta(l, p) &\leq \frac{2Y}{a} l^{\frac{\log l}{\log \omega}} = O\left(\frac{1}{a} l^{\frac{\log l}{\log \omega}} p^{-\frac{1-\beta}{2}} \log p\right) \\ &= O\left(l^{-\frac{1-\beta}{2} + \frac{\log 8}{\log \omega}} p^{-\frac{1}{2}} \omega \log^3 p\right) \\ l^{1-\beta} &= O\left(l^{\frac{1+\beta}{2} + \frac{\log 8}{\log \omega}} \omega \log^3 p\right) \end{aligned}$$

or,

$$(15) \quad \beta \geq \frac{1}{2} + O\left(\frac{1}{\log \omega}\right) + O\left(\frac{\log \omega}{\log l}\right) + O(1)$$

Secondly, we assume that no residue class (*mod*  $a$ ) contains more than  $\omega$  of the numbers  $au$ . Hence there are at least  $\frac{t_1}{\omega}$  different residue classes (*mod*  $a$ )

which contain a number  $au$ . Applying Lemma 4, we can find a number  $N$  of the form,

$$N = au_1 + \dots + au_s$$

which is a sum of  $s$   $k$ th power residues (mod  $p$ ) and satisfies

$$\frac{Y}{a} < N \leq \frac{2Y}{a}$$

where 
$$Y = O\left(\left(\omega \frac{a \log \log a}{t_1}\right) = O\left(\omega \frac{a}{t} \log^2 p\right)\right)$$

since 
$$t_1 \geq \frac{t}{4 \log^2 p}$$

Applying Lemma 2 (ii) with  $d=N$  we have

$$(16) \quad \delta(k, p) \leq \frac{4Y}{a} s, s^{\frac{\log p}{\log Y}} = O\left(X, \frac{\log t}{\log \frac{Y}{a}} \omega \log^2 p\right)$$

since 
$$s = O\left(\frac{\omega \log^2 p}{t}\right).$$

We have 
$$p = k^{1+\rho}, a \leq Y \frac{8 \log \log p}{t}, Y \leq X. \text{ Hence}$$

$$(17) \quad s = O\left(\omega \frac{a}{t} \log^2 p\right) = O\left(\omega \frac{X}{p} \frac{8 \log \log p}{\log \log p} t^{-2} \log^2 p\right) \\ = O\left(\omega \frac{p}{k} \frac{1-\beta}{2} \frac{8}{p \log k \log t^{-2} \log^2 p}\right) = O\left(k^{\frac{1+\beta}{2}-\rho} \frac{24}{\log \log p} \omega \log^2 p\right)$$

and

$$(18) \quad \frac{Ys}{a} \geq \frac{Y}{a} \geq t \frac{8}{p \log \log p} \geq k^{\rho} \frac{24}{\log \log p}$$

From (16), (17) and (18) it follows that

$$\delta(k, p) = O\left(k^{\frac{1+\beta}{2}} k^{\left(\frac{1+\beta}{2}-\rho\right)} \left(\frac{1+\rho}{p}\right) + O\left(\frac{\log \omega}{\log k}\right) + O(1)\right) \omega \log^2 p$$

or,

$$1-\beta \leq \frac{1+\beta}{2} + \frac{(1+\rho)(1+\beta)}{2\rho} - (1+\rho) + O\left(\frac{\log \omega}{\log k}\right) + O(1),$$

$$\beta \left(2 + \frac{1}{2\rho}\right) \geq 1+\rho - \frac{1}{2\rho} + O\left(\frac{\log \omega}{\log k}\right) + O(1),$$

$$\beta \geq \frac{2\rho^2 + 2\rho - 1}{4\rho + 1} + O\left(\frac{\log \omega}{\log p}\right) + o(1)$$

$$(19) \quad \beta \geq \frac{1}{2}\rho + \frac{1}{2} - \frac{11}{8(4\rho + 1)} + O\left(\frac{\log \omega}{\log p}\right) + o(1)$$

For  $\frac{\sqrt{3}-1}{2} < \rho \leq \frac{1}{2}$  we have  $0 < \frac{1}{2}\rho + \frac{1}{2} - \frac{11}{8(4\rho + 1)} < 1$ . This and the inequalities (14) (15) and (19) give

$$\lim_{p \rightarrow \infty} \beta \geq \text{Min}\left(\frac{1}{2}\rho + \frac{1}{2} - \frac{11}{8(4\rho + 1)}\right) \text{ uniformly in } p \text{ for } \frac{\sqrt{3}-1}{2} < \rho \leq \frac{1}{2}$$

Hence Theorem 2

### SECTION 6 PROOF OF THEOREM 3

We write

$$b(k, l) = k^{1-\beta} O(\beta < 1)$$

$$p = t/l + 1 = l^{1+\rho} \quad t \geq 3$$

$$\text{Let } 0 < \rho \leq \frac{\sqrt{641}-5}{44} \quad \text{Theorem 1 gives}$$

$$(20) \quad \lim_{k \rightarrow \infty} \beta > 1 - \frac{\log p}{\log l} = 1 - (1+\rho) = \frac{1}{2} - \rho$$

$$\geq \left(\frac{1}{2} - \rho\right)_{\rho = \frac{\sqrt{641}-5}{44}} = \frac{103-3\sqrt{641}}{220}$$

$$\text{Let } \frac{\sqrt{641}-5}{44} \leq \rho \leq \frac{1}{2} \quad \text{Theorem 2 gives}$$

$$(21) \quad \lim_{k \rightarrow \infty} \beta \geq \frac{103-3\sqrt{641}}{220}$$

Since

$$\text{Min}\left(\frac{1}{2}\rho + \frac{1}{2} - \frac{11}{8(4\rho + 1)}\right) = \left(\frac{1}{2}\rho + \frac{1}{2} - \frac{11}{8(4\rho + 1)}\right)_{\rho = \frac{\sqrt{641}-5}{44}}$$

$$= \frac{103-3\sqrt{641}}{220}$$

Let  $\rho > \frac{1}{2}$ . We have

$$\frac{M(p, n, s)}{p^{s-1}} = 1 + p^{-s} \sum_{1 \leq a < p} (S_a, p)^s e^{-\frac{2\pi i a n}{p}}$$

Since\*

$$|S_{a,p}| \leq (k-1) \sqrt{p}$$

it follows that

$$\begin{aligned} \left| p^{-1} \sum_{1 \leq a < p} (S_{a,p})^r e^{-2\pi i a n/p} \right| &< p^{-1} p^{k^r} p^{-\frac{r}{2}} = p^{1-\frac{r}{2}} k^r \\ &= k^{1+r-\frac{r}{2}(\rho-1)} \end{aligned}$$

$M(p, n, s) > 0$  if

$$s \geq \frac{2\rho+2}{\rho-1} = 2 + \frac{4}{\rho-1}$$

Hence if  $\rho > 1$ ,

$$(22) \quad \delta(k, \rho) \leq \begin{cases} 2 + \frac{4}{\rho-1} & \text{if } \frac{4}{\rho-1} \text{ is an integer} \\ 3 + \left[ \frac{4}{\rho-1} \right] & \text{otherwise} \end{cases}$$

For instance, if  $\geq \rho^{\frac{1}{2}}$  we get

$$\delta(k, \rho) \leq 18$$

This and (20) and (21) give Theorem 3

#### SECTION 7. LEMMAS FOR THE PROOF OF THEOREM 4

LEMMA 8†. Let  $k = p^v k_0$ ,  $p \geq 2$ ,  $v \geq 0$ ,  $p/k_0$  and let

$$v = \begin{cases} v+2 & \text{if } p=2, \\ v+1 & \text{if } p>2. \end{cases}$$

Then if  $l \geq v$ ,

$$\Gamma(k, p^l) = \Gamma(k, p^v)$$

Proof. Every residue class ( $\text{mod } p^l$ ) which is prime to  $p$  and a  $l$ th power residue ( $\text{mod } p^v$ ) is also a  $l$ th power residue ( $\text{mod } p^l$ ).

LEMMA 9. Let  $k_1 = p^v \frac{p-1}{t}$ ,  $p \geq 5$ ,  $v \geq 1$ ,  $t/p-1$ ,  $t > 2$ .

Then there exists an integer  $hp^a$  with  $p/h \leq a \leq v$  such that

$$\Delta(k_1, p^{v+1}, hp^a) \leq 2 \{p^{\frac{1}{2}}\}$$

\*Landau, *Vorlesungen über Zahlentheorie*, Bd. 1, Satz 811

†This lemma follows from Lemma 5 in P. V. 4. Or see J. Landau, *Vorlesungen über Zahlentheorie*, Bd. 1, Satz 291



Proof. We shall first show that

$$(23) \quad R \equiv xy^{-1} \pmod{p^{v+1}}$$

is soluble with  $1 \leq y, < p, p \nmid x, |x| \leq p^v, (x, y) = 1, |x| > y$  where  $R$  is a suitably chosen  $k_1$ th power residue  $\not\equiv \pm 1 \pmod{p^{v+1}}$  and prime to  $p$ .

Since  $t > 2$ , we can find a  $k_1$ th power residue  $R_1 \not\equiv \pm 1 \pmod{p^{v+1}}$  and prime to  $p$ . We consider the least positive residue  $\pmod{p^{v+1}}$  of  $m R_1$  for  $1 \leq m \leq p-1$ . Then the numbers

$$0, R_1, 2R_1, \dots, (p-1)R_1, p^{v+1}$$

define  $p+1$  points distributed among the  $p$  intervals

$$r(p^v+1) \leq x < (r+1)(p^v+1) \quad (0 \leq r \leq p-1)$$

At least one interval must contain two points; hence we can find  $x_1, y_1$  such that

$$y_1 R \equiv x_1 \pmod{p^{v+1}}$$

where

$$1 \leq y_1 \leq p-1, |x_1| \leq p^v.$$

We may assume without loss of generality that  $|x_1| > y_1$  since otherwise we can substitute  $R_1^{-1}$  for  $R_1$  in the argument. Since  $1 \leq y_1 \leq p-1, p/y_1$ , we may assume therefore that  $(x_1, y_1) = 1$ .

If  $|x_1| > p^{\frac{1}{2}}$ , then  $R = R_1, x = x_1, y = y_1$  satisfy the required conditions.

If  $|x_1| < p^{\frac{1}{2}}$ , we can find a positive integer  $f$  such that

$$\frac{p}{p^{\frac{1}{2}}} = p^{\frac{1}{2}} < |x_1| \leq p,$$

and since  $y_1^f < |x_1| \leq p, (x_1^f, y_1^f) = 1$  it follows that (23) is soluble with  $R = R_1^f, x = x_1^f, y = y_1^f$ .

Now we consider the numbers

$$(24) \quad v + R w \quad (0 \leq v, w \leq [p])$$

where  $R$  is defined by (23).

If any two of these numbers, say,  $v_1 + R w_1, v_2 + R w_2$ , were congruent  $\pmod{p^{v+1}}$ , we should have

$$R \equiv xy^{-1} \equiv (v_1 - v_2)(w_1 - w_2)^{-1},$$

or,

$$x(w_1 - w_2) - y(v_1 - v_2) = 0$$

since

$$|x(w_1 - w_2) - y(v_1 - v_2)| < p^v p^{\frac{1}{2}} + (p-1)p^{\frac{1}{2}} < p^{v+1}$$

It follows that  $x/v_1 - v_2$  since  $(x, y) = 1$ . But  $|x| > p^{\frac{1}{2}} > |v_1 - v_2|$ . Hence  $v_1 = v_2$ , consequently  $w_1 = w_2$ .

Thus (24) defines  $([p^{\frac{1}{2}}] + 1)^2 \geq p + 1$   
 mutually incongruent numbers (mod  $p^{v+1}$ ). Hence we can find two numbers, say,  
 $n_1$  and  $n_2$ , from (24), such that

$$\begin{aligned} n_1 - n_2 &\equiv 0 \pmod{p}, \\ n_1 - n_2 &\not\equiv 0 \pmod{p^{v+1}}. \end{aligned}$$

We write  $n_1 - n_2 = hp^a$ . Then  $1 \leq a \leq v$ ,  $p/h$  and

$$\Delta(k_1, p^{v+1}, hp^a) \leq 2[p^{\frac{1}{2}}]$$

Hence the lemma

LEMMA 10 Let  $k_1 = p^v \frac{p-1}{t}$ ,  $v \geq 0$ ,  $t/p-1$ ,  $t > 2$ .

Then for every positive  $E$  and  $\delta > \frac{1}{2}$ ,

$$\Delta(k_1, p^{v+1}) = O(p^{\delta v} \left(\frac{p-1}{t}\right)^{1-C+E})$$

provided  $p \geq 5$  and  $p$  satisfies the inequality

$$1 + 2[p^{\frac{1}{2}}] \leq p^{\delta}$$

Proof. The proof is by induction on  $v$ . Let  $v=0$ ; since  $t > 2$ , the lemma follows from Theorem 3 and

$$\Delta(k_1, p) \leq \Gamma(k_1, p) \leq \delta(k_1, p) + 1.$$

Let  $v \geq 1$  and suppose that the lemma is true for  $v' < v$ . Then we write,

$$(25) \quad \Delta(p^{v'} \frac{p-1}{t}, p^{v+1}) \leq Bp^{\delta v} \left(\frac{p-1}{t}\right)^{1-C+E}$$

where  $B=B(\varepsilon)$  depends on  $\varepsilon$  only

By Lemma 9 we can find an integer  $hp^a$  with  $p/h$ ,  $1 \leq a \leq v$  such that

$$(26) \quad \Delta(k_1, p^{v+1}, hp^a) \leq 2[p^{\frac{1}{2}}].$$

Since  $p/h$ , we can find an integer  $v$  such that for any integer  $n$ ,

$$(27) \quad np^a \equiv hp^a \pmod{p^{v+1}}$$

We have for  $1 \leq \mu \leq v$ ,  $p/h$ ,

$$(28) \quad x^{p^\mu} \equiv x^{h p^\mu - 1} \pmod{p^{v+1}}$$

Hence (25) and (28) give

$$(29) \quad \left\{ \begin{aligned} \Delta(k_1, p^a) &= \Delta(p^{a-1} \frac{p-1}{t}, p^a) \leq Bp^{(a-1)\delta} \left(\frac{p-1}{t}\right)^{1-C+E} \\ \Delta(k_1, p^{v+1-a}) &= \Delta(p^{v-a} \frac{p-1}{t}, p^{v+1-a}) \leq Bp^{(v-a)\delta} \left(\frac{p-1}{t}\right)^{1-C+E} \end{aligned} \right.$$

Applying (26), (27) and (29) it follows that for every integer  $n$ ,

$$\Delta(k_1, p^{v+1}, np^e) \leq 2B[p^{\frac{1}{2}}]p^{(v-a)\delta} \left(\frac{p-1}{t}\right)^{1-C+E}$$

This and (29) give

$$\begin{aligned} \Delta(k_1, p^{v+1} \leq Bp)^{(a-1)\delta} \left(\frac{p-1}{t}\right)^{1-C+E} &+ 2B[p^{\frac{1}{2}}]p^{(v-a)\delta} \left(\frac{p-1}{t}\right)^{1-C+E} \\ &\leq B \left(\frac{p-1}{t}\right)^{1-C+E} (p^{w-1}\delta + 2[p^{\frac{1}{2}}]p^{(v-1)\delta}) \\ &= Bp^{\delta v} \left(\frac{p-1}{t}\right)^{1-C+E} (p^{-\delta} + 2[p^{\frac{1}{2}}]p^{-\delta}) \\ &\leq Bp^{\delta v} \left(\frac{p-1}{t}\right)^{1-C+E} \\ &\quad \text{if } p^{\delta} \geq 1 + 2[p^{\frac{1}{2}}] \end{aligned}$$

This proves the lemma.

LEMMA 11. Let  $k_1 = p^v \cdot \frac{p-1}{t}$ ,  $p \geq 7$ ,  $v \geq 0$ ,  $t/p-1$ ,  $t > 2$ .

Then for every positive  $E$ ,

$$\Gamma(k_1, p^{v+1}) = O(k_1^{1-C+E})$$

Proof We have,

$$1-C = \frac{117+3\sqrt{641}}{220} > \frac{192.951}{220} > \frac{19.294}{22} = 875 + .002 = \frac{7}{8} + \frac{1}{500}.$$

We have

$$7^7 = (5+2)^7 > 5^7 + 14 \cdot 5^6 + 84 \cdot 5^5 > 5 \cdot 5^7 = 5^8.$$

Let  $p=7$ . Then

$$p^{1-C} = 7^{1-C} > 7^{\frac{1}{2}} > 5 = 1 + 2[7^{\frac{1}{2}}] = 1 + 2[p^{\frac{1}{2}}].$$

Let  $p \geq 11$ . We have,

$$8^8 \cdot 11^8 = (8^3 11)^3 \cdot 8^3 > (2 \cdot 7^2)^3 \cdot 7 = 2^6 \cdot 7^7 > 7^8$$

$$p^{1-C-\frac{1}{2}} > 11^{\frac{1}{2}} > \frac{1}{2} = 2 + \frac{1}{2} > 2 + \frac{1}{p^{\frac{1}{2}}}.$$

Hence

$$p^{1-C} > 1 + 2p^{\frac{1}{2}} > 1 + 2[p^{\frac{1}{2}}] \text{ if } p \geq 7$$

It now follows from Lemma 10 with  $\delta = 1-c$  that

$$(30) \quad \Delta(k_1, p^{v+1}) = O(k_1^{1-C+E}) \text{ if } p \geq 7, v \geq 0.$$

Let  $g$  be a primitive root ( $\text{mod } p^{v+1}$ ) Then

$$-1 \equiv g^{t^1} + g^{t^2} + \dots + g^{t^{t-1}} \pmod{p^{v+1}}$$

Hence

$$(31) \quad \Gamma(k_1, p^{v+1}) \leq (t-1)\Delta(k_1, p^{v+1})$$

If  $v=0$ , the lemma follows from Theorem 3 and

$$\Gamma(k_1, p) \leq \delta(k_1, p) + 1$$

Let  $v \geq 1$ . We consider the following cases

I.  $v=1, t < p^{\frac{1}{2}}$ .

In the proof of Lemma 9 it is shown that if  $v \geq 1$ , we can find a  $k_1$ th power residue  $R \not\equiv \pm 1 \pmod{p^{v+1}}$  and prime to  $p$  such that

$$R \equiv xy^{-1} \pmod{p^{v+1}}$$

where

$$1 \leq y < p, y < |x| \leq p^v, (x, y) = 1$$

Put  $v=1$ . Then the following sub-cases are considered

(i)  $|x| < p^{\frac{1}{2}}$ , (ii)  $p^{\frac{1}{2}} < |x| < p^{\frac{1}{2}}$ , (iii)  $p^{\frac{1}{2}} < |x| \leq p$

Now we apply a similar argument as in the proof of Theorem 1 to show that

$$\Gamma(k_1, p^2) = O(p^{\frac{1}{2}})$$

In sub-cases (i) and (iii) we have at least  $\frac{p^{\frac{1}{2}}}{4}$  mutually incongruent numbers ( $\text{mod } p^2$ ) which are sums of at most  $p^{\frac{1}{2}}$   $k_1$ th power residues ( $\text{mod } p^2$ ). At least  $\frac{p^{\frac{1}{2}}}{4} - p$  of these numbers are prime to  $p$ . In sub-case (ii) we have at least  $\frac{p^{\frac{1}{2}}}{27} - p$  mutually incongruent numbers ( $\text{mod } p^2$ ), which are all prime to  $p$  and sums of at most  $p^{\frac{1}{2}}$   $k_1$ th power residues ( $\text{mod } p^2$ ). In each sub-case, repeated application of Lemma 3 gives

$$\Gamma(k_1, p^2) = O(p^{\frac{1}{2}})$$

We have  $\frac{p-1}{t} > \frac{1}{2}p^{\frac{1}{2}}$ . Hence

$$\Gamma(k_1, p^2) = O(p^{\frac{1}{2}}) = O(p^{\frac{1}{2} + \epsilon}) = O(p^{\frac{1}{2}} \left( \frac{p-1}{t} \right)^{\epsilon}) = O(k_1^{1-C+E})$$

II.  $v \geq 2, t < p^{\frac{1}{2}}$ . We have

$$\frac{1}{2}v + \frac{1}{2} < \frac{1}{2}v < (1-C)v \quad \text{if } v \geq 2.$$

It follows from (31) and Lemma 10 with  $\delta = \frac{1}{2}$  that

$$\Gamma(k_1, p^{v+1}) = O(p^{\frac{1}{2}v + \frac{1}{2}} \left( \frac{p-1}{t} \right)^{1-C+E}) = O(k_1^{1-C+E})$$

if  $p \geq C_1$ , where  $C_1$  is an absolute constant

If  $7 \leq p < c_1$  we have  $t \leq p-1 < c_3$ . Hence by (30) and (31)

$$\Gamma(k_1 p^{v+1}) < c_3 \quad \Delta(k_1 p^{v+1}) = O(k_1^{1-C+E})$$

III  $v \geq 1 \quad t > p^{\frac{1}{2}}$

Then  $p > \left(\frac{p-1}{t}\right)^{\frac{1}{2}}$ . It is easily seen from (22) and (28) that  $-1 \pmod{p}$  is representable as  $x_1^{t_1} + \dots + x_p^{t_p}$  where all the  $x$ 's are prime to  $p$  and  $s = O(1)$ . Or

$$(32) \quad -1 = x_1^{t_1} + \dots + x_p^{t_p} + fp \quad s = O(1)$$

Now if in (32)  $p^v/f$  then

$$\Gamma(k_1 p^{v+1} - 1) = O(1)$$

and our result would follow from (30)

Otherwise we can write  $-fp = hp^a$  in (32). Then  $p/h \leq a \leq v$  and

$$(33) \quad \Gamma(k_1 p^{v+1} hp^a) = O(1).$$

Now we apply the same argument as in Lemma 10 but with (33) instead of (26) and put  $\delta = 1 - c$ . Then it is easily seen that

$$\Gamma(k_1 p^{v+1}) = O(k_1^{1-C+E})$$

if  $p \geq c_4$  where  $c_4$  is an absolute constant.

If  $7 \leq p < c_4$  we have  $t \leq p-1 < c_4$ . The required result now follows from (30) and (31).

This completes the proof of the lemma.

LEMMA 12. Let  $2/k$ . Then

$$\Gamma(k, 5^l) = O(k^{\frac{1}{2}}) \quad (l \geq 1)$$

Proof. We write

$$k = 5^v k_0 \quad 5/k_0 \quad 2/k_0 \quad v \geq 0$$

By Lemma 8 it is sufficient to prove that

$$\Gamma(k, 5^{v+1}) = O(k^{\frac{1}{2}})$$

If  $v = 0$  we have

$$\Gamma(k, 5) \leq 5$$

Let  $v \geq 1$ . Let  $g$  be a primitive root  $\pmod{5^{v+1}}$ . We write

$$R = g^k$$

Then  $R$  is a  $k$ th power residue  $\not\equiv \pm 1 \pmod{5^{v+1}}$ ,

$5/R$  and

$$R^2 \equiv -1 \pmod{5^{v+1}}$$

We consider the numbers

$$v + wR \quad \left( 0 \leq v, w < \frac{5^{\frac{v+1}{2}}}{2} \right).$$

If any two of these numbers, say,  $v_1 + w_1 R$ ,  $v_2 + w_2 R$  were congruent (*mod*  $5^{v+1}$ ), we should have

$$\begin{aligned} v_1 - v_2 &\equiv (w_1 - w_2) R, \\ (v_1 - v_2)^2 + (w_1 - w_2)^2 &\equiv 0 \end{aligned}$$

Since

$$|(v_1 - v_2)^2 + (w_1 - w_2)^2| < \frac{2 \cdot 5^{v+1}}{4} < 5^{v+1},$$

it follows that

$$(v_1 - v_2)^2 + (w_1 - w_2)^2 = 0$$

Hence  $v_1 = v_2$ ,  $w_1 = w_2$ .

Hence there are  $\binom{v+1}{2} + 1 > \frac{5^{v+1}}{4}$  mutually incongruent numbers

(*mod*  $5^{v+1}$ ) which are sums of at most  $5^{\frac{v+1}{2}}$   $5^{\frac{v+1}{2}}$ th power residues (*mod*  $5^{v+1}$ ). At least  $\frac{5^{v+1}}{4} - 5^v = \frac{5^v}{4}$  of these numbers are prime to 5. Repeated application of Lemma 3 gives

$$\Gamma(k, 5^{v+1}) \leq 5^{\frac{v+1}{2}} \left( \left\lfloor \frac{5^{v+1}}{5^v} \right\rfloor + 1 \right) = O(5^{\frac{v}{2}}) = O(k^{\frac{1}{2}})$$

which proves the lemma.

#### Section 8. Proof of Theorem 4.

As before  $c = \frac{103 - 3\sqrt{641}}{220}$ ,  $\varepsilon$  denotes an arbitrarily small positive number.

Let  $k = p^v k_0$ ,  $p \geq 2$ ,  $v \geq 0$ ,  $p/k_0$ . We write

$$v = \begin{cases} v+2 & \text{if } p=2 \\ v+1 & \text{if } p>2. \end{cases}$$

Let  $p > 2$  and let  $g$  be a primitive root (*mod*  $p^{v+1}$ ). We write

$$\begin{aligned} (k, \phi(p^{v+1})) &= k_1, \\ p^v(p-1) &= k_1 t, \\ k &= k_1 k_2 = p^v \frac{p-1}{t}, \quad k_2. \end{aligned}$$

If  $(n, p) = 1$ ,

$$\begin{aligned} n &\equiv g^b \pmod{p^{v+1}}, \quad 1 \leq b \leq p^v(p-1), \\ n^{k_1} &\equiv g^{b k_1 + r p^v(p-1)} \equiv g^{k_1(b + r t)} \end{aligned}$$

for every integer  $r$ . Since  $(t, k_2) = 1$  we can choose  $r$  so that  $b + r t \equiv 0 \pmod{k_2}$ .

Also if  $p/n$ ,

$$n^{k_1} \equiv 0 \pmod{p^{v+1}}$$

since  $k_1 = p^v \cdot \frac{p-1}{t} \geq p^v \geq v+1$  for  $p > 2, v \geq 0$ . Hence

$$(34) \quad \Gamma(k, p^{v+1}) = \Gamma(k_1, p^{v+1}) = \Gamma(p^v \frac{p-1}{t}, p^{v+1}).$$

Applying Lemma 8 it follows that

$$\Gamma(k, p^l) = \Gamma(k, p^{v+1}) = \Gamma(p^v \frac{p-1}{t}, p^{v+1}) \text{ if } l \geq v+1$$

This and Lemmas 11 and 12 give

$$\Gamma(l, p^l) = O((k, \phi(p^{v+1}))^{l(v+1)}) = O(l^{l(v+1)})$$

if  $p \geq 5, \frac{1}{2}(p-1)/k, l \geq 1$  which is Theorem 4A

Proof of Theorem 4B

Let  $p > 2$ . Applying (34) it is easy to see that\*

$$(35) \quad \Gamma(k, p^{v+1}) = \Gamma(p^v \frac{p-1}{t}, p^{v+1}) = \begin{cases} p^{v+1} & \text{if } p \geq 3, v \geq 0, t=1 \\ \frac{1}{2}(p^{v+1}-1) & \text{if } p \geq 5, v \geq 0, t=2 \\ \frac{1}{4}(p^{v+1}-1) & \text{if } p=3, v \geq 1, t=2. \\ 2 & \text{if } p=3, v=0, t=2. \end{cases}$$

Also if  $k > 2$ ,

$$(36) \quad \Gamma(k, 2^{v+1}) = \begin{cases} 2 & \text{if } v=0. \\ 2^{v+1} & \text{if } v > 0. \end{cases}$$

By Lemma 8, we have

$$(37) \quad \Gamma(k) = \max_{p \geq 2} \Gamma(k, p^v)$$

Theorem 4B is an immediate consequence of Theorem 4A and (35), (36), (37).

\* See P. N. 8, Lemma 7 for the results stated in (35) and (36).

# ON FORMULÆ IN PARTITIONS AND DIVISORS OF A NUMBER, DERIVED FROM SYMMETRIC FUNCTIONS

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1 In the paper on 'Recurrence formulæ for Bernoulli's numbers' the author has used symmetric functions and determinants to investigate recurrence formulæ for the Bernoullian numbers.

Following the methods and notation explained in that paper,\* formulæ in partitions and divisors of an integer can be easily established, as is shown in this paper.

$$\begin{aligned} 2. \text{ Let } f(x) &= (1-x)(1-x^2)(1-x^3) \dots \\ &= 1 + \sum_{n=1}^{\infty} (-1)^n [x^{\frac{1}{2}n(3n-1)} + x^{\frac{1}{2}n(3n+1)}] \\ &= 1 - x - x^2 + x^5 + x^7 - x^{12} - x^{15} + x^{22} + x^{27} \dots \end{aligned}$$

Comparing it with

$f(x) = 1 - a_1x + a_2x^2 - a_3x^3 + \dots + (-1)^r a_r x^r + \dots$ , where  $a_r$ 's are the elementary symmetric functions, we have:  $a_1 = 1, a_2 = -1, a_3 = a_4 = 0, a_5 = -1$ , etc.

$a_r = 0$  if  $r$  is not of the form  $\frac{1}{2}n(3n \pm 1)$

and  $(-1)^{r-n}$  if  $r$  is of the form  $\frac{1}{2}n(3n \pm 1)$ .

$$\text{Since } \frac{1}{(1-x)(1-x^2)(1-x^3) \dots} = \sum p(n) x^n$$

where  $p(n)$  denotes the number of partitions of the integer  $n$ , and also

$$\frac{1}{f(x)} = \sum h_n x^n,$$

where  $h_n$  denotes the aleph symmetric functions, we get by comparison

$$h_n = p(n).$$

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\*M. Ziaud Din, *Math. Student*, Vol. 3, (1-11).



3 Consider the well-known determinant

$$S_n = \begin{vmatrix} a_1 & 1 & 0 & 0 & 0 & . & 0 \\ 2a_2 & a_1 & 1 & 0 & 0 & . & 0 \\ 3a_3 & a_2 & a_1 & 1 & 0 & . & 0 \\ - & - & - & - & - & . & 0 \\ - & - & - & - & - & . & 0 \\ na_n & - & - & - & - & . & 1 \end{vmatrix}$$

where  $S_n$  is the sum of the  $n^{\text{th}}$  powers of the roots of  $(1-x)(1-x^2)(1-x^3) \dots$ . Substituting the numerical values of  $a_1, a_2, a_3, \dots$  as given in Art. 2, we obtain from the above determinant

$S_2 = \text{sum of the squares of the roots} = 3 = \text{sum of divisors of } 2 = \sigma(2).$

$S_3 = \text{sum of the cubes of the roots} = 4 = \text{sum of divisors of } 3 = \sigma(3).$

$S_4 = \text{sum of the fourth powers of the roots} = 7 = \text{sum of divisors of } 4 = \sigma(4),$   
and so on.

Thus we have numerically

$$S_n \equiv \sigma(n)$$

4. Expand the determinant in Art. 3, in terms of the elements of the first column, and following the notation of my paper cited in Art. 1, we obtain

$$S_n = a_1 \{1^{\overline{n-1}}\} - 2a_2 \{1^{\overline{n-2}}\} + 3a_3 \{1^{\overline{n-3}}\} - 4a_4 \{1^{\overline{n-4}}\} + \dots$$

$$= a_1(n-1) - 2a_2(n-2) + 3a_3(n-3) - 4a_4(n-4) + \dots$$

Since  $S_n = \sigma(n)$ ;  $h_n = (n) = p(n)$  and the numerical values of  $a_r$  are known, therefore we obtain the formula,

$$\sigma(n) = p(n-1) + 2p(n-2) - 5p(n-5) - 7p(n-7) + \dots$$

The series will cease when any  $(n-r)$  is negative as  $p(-k)$  is to be taken 0 and  $p(1)=1$ .

[This formula is due to Catalan (Dickson, *History*, Vol. I, p. 290), but Macmahon refers it to Euler in *Combinatory Analysis* II, p. 57].

Applying the general principle indicated above, other formulæ can similarly be derived from the above determinant, from its various expansions, e.g., if the first column is replaced by the second column, the expansion gives  $0 = p(n-1) - p(n-2) - p(n-3) + \dots + (-1)^r a_r p(n-r-1) + \dots$

From this we deduce

$$p(n) - p(n-1) - p(n-2) + p(n-5) + \dots = 0,$$

which is Euler's formula<sup>1</sup> Euler's formula also follows immediately from Wronski's relation

$$h_n - a_1 h_{n-1} + a_2 h_{n-2} - a_3 h_{n-3} + \dots + (-1)^r a_r h_{n-r} + \dots = 0.$$

5. Following the above theory, some well-known formulæ in symmetric functions and determinants at once yield results in partitions and divisors

From Newton's formula

$$S_n - S_{n-1} a_1 + S_{n-2} a_2 - S_{n-3} a_3 + \dots + (-1)^n n a_n = 0,$$

we obtain Euler's formula<sup>2</sup>

$$\sigma(n) - \sigma(n-1) + \sigma(n-2) + \sigma(n-5) + \dots = 0$$

or  $(-1)^{r-1} n$ ; according as  $n$  is not or is of the form  $\frac{1}{2} r (3r \pm 1)$

$\sigma(0)$  is taken as zero.

From the well-known determinantal relation,

$n! h_n =$	$S_1$	$-1$	$0$	$0$	$0$
	$S_2$	$S_1$	$-2$	$0$	$0$
	$S_3$	$S_2$	$S_1$	$-3$	$0$
	$—$	$—$	$—$	$—$	$—$
	$—$	$—$	$—$	$—$	$—$
	$S_n$	$S_{n-1}$	$—$	$—$	$S_1$

we obtain	$1$	$-1$	$0$	$0$	$0$
	$3$	$1$	$-2$	$0$	$0$
	$4$	$3$	$1$	$-3$	$0$
	$\dots$	$\cdot$	$\cdot$	$\cdot$	$\cdot$
	$\sigma(n)$	$—$	$—$	$—$	$1$

From Briochi's relation

$$S_n + h_1 S_{n-1} + h_2 S_{n-2} + \dots + h_n S_1 = n h_n$$

we derive

$$\begin{aligned} \sigma(n) + \sigma(n-1) + p(2) \sigma(n-2) + p(3) \sigma(n-3) \\ + \dots + p(n-1) = n p(n) \end{aligned}$$

which connects the divisors and partitions.

<sup>1</sup> Dickson, II, p. 105.

<sup>2</sup> Glaisher, *Proc Camb Phil Soc*, Vol. 5, Part II (1884), p. 108.

A referee remarks that the final formula may be obtained directly as follows —

Logarithmic differentiation of

$$\frac{1}{(1-x)(1-x^2)\dots} = \sum_0^{\infty} p(x) x^n; |x| < 1$$

$$\text{gives } \sum_1^{\infty} \sigma'(n) x^n = \sum_1^{\infty} n p(n) x^n \bigg/ \sum_1^{\infty} p(n) x^n$$

Cross-multiplication and equating co-efficients of  $x^n$ , on both sides, gives the desired result.

# OPERATIONAL CALCULUS AND INFINITE INTEGRALS

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Communicated by Dr R S Verma

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1 The object of this paper is to investigate a few new infinite integrals by applying Goldstein Parseval theorem in Operational Calculus to operational relations recently given by various authors

The form in which Goldstein\* has restated Parseval's theorem is that if

$$f_1(p) = \phi_1(x) \text{ and } f_2(p) = \phi_2(x)$$

then provided that the integrals converge

$$\int_0^{\infty} \frac{f_1(x) \phi_2(x)}{x} dx = \int_0^{\infty} \frac{f_2(x) \phi_1(x)}{x} dx$$

2 *Result 1* It is easy to see on term-by-term interpretation with the help of the relation ‡

$$\Gamma(n+1) p^{-n} = x^n \quad R(n) > -1$$

that for  $p > k$

$$\frac{p^\lambda}{(p^2 + k^2)^\mu} = \frac{1}{p^{2\mu - \lambda - 1}} {}_1F_0\left(\mu, -\frac{k^2}{p^2}\right) = \frac{x^{2\mu - \lambda}}{\Gamma^2(2\mu - \lambda + 1)} {}_1F_2\left(\mu, \mu + \frac{1-\lambda}{2}, \mu + 1 - \frac{1}{2}\lambda, -\frac{1}{4}k^2 x^2\right) \quad (2.1)$$

$$R(2\mu - \lambda + 1) > 0$$

By the principle of analytic continuation the relation (2.1) holds for  $p > 0$

Applying Parseval-Goldstein theorem to the above relation and the following due to Howell§

My best thanks are due to Dr R. S. Verma D Sc for suggesting the problem

\*R. Goldstein Proc Lond Math Soc (2) 34 (1932) pp 103 125

‡This symbol implies that

$$f_1(p) = \int_0^{\infty} e^{-px} \phi_1(x) dx \quad p > 0$$

§P. Humbert, Calcul Symbolique (Paris 1934), henceforth referred to as C S

§W. T. Howell Phil Mag. (7) 24 (1935) p 107

$$\Gamma(\nu + \frac{1}{2}) p D_{-\nu-\frac{1}{2}}(pe^{\frac{1}{2}\pi i}) D_{-\nu-\frac{1}{2}}(pe^{-\frac{1}{2}\pi i}) \doteq \sqrt{\pi} J_{\nu}(\frac{1}{2}x^2), \quad R(\nu) > -\frac{1}{2} \quad (2'2)$$

we have

$$I_1 \equiv \frac{\Gamma(\nu + \frac{1}{2})}{\sqrt{\pi} \Gamma(\frac{1}{2}\mu - \lambda + 1)} \int_0^{\infty} x^{2\mu-\lambda} D_{-\nu-\frac{1}{2}}(xe^{\frac{1}{2}\pi i}) D_{-\nu-\frac{1}{2}}(xe^{-\frac{1}{2}\pi i}) \times \\ {}_1F_2\left(\mu, \mu + \frac{1-\lambda}{2}, \mu + 1 - \frac{1}{2}\lambda, -\frac{k^2 x^2}{4}\right) dx = \int_0^{\infty} x^{\lambda-1} J_{\nu}(\frac{1}{2}x^2) (x^2 + k^2)^{-\mu} dx.$$

Evaluating the latter integral by a known formula,\* we have

$$I_1 = \frac{\Gamma(\frac{1}{2}\lambda + \nu) \Gamma(\frac{1}{2}\mu - \frac{1}{2}\lambda - \nu)}{\Gamma(1 + \nu) \Gamma(\frac{1}{2}\mu)^{2\nu+1}} k^{\lambda+2\nu-2\mu} \\ {}_2F_3\left(\nu + 1, \frac{1}{2}\lambda + \frac{1}{2}\nu, \frac{1}{2}\lambda + \frac{1}{2}(\nu + 1), 1 + \frac{1}{2}\lambda + \frac{1}{2}(\nu - \mu), -\frac{1}{4}k^4\right) + \\ + \frac{\Gamma(\frac{1}{2}\lambda + \frac{1}{2}\nu - \frac{1}{2}\mu) 2^{\lambda-2\mu-2}}{\Gamma(1 + \frac{1}{2}\nu + \frac{1}{2}\mu - \frac{1}{2}\lambda)} {}_2F_3\left(\frac{1}{2}, 1 + \frac{1}{2}(\mu - \nu) - \frac{1}{2}\lambda, 1 + \frac{1}{2}(\mu + \nu) - \frac{1}{2}\lambda, -\frac{1}{4}k^4\right) - \\ - \frac{k^2 \mu \Gamma(\frac{1}{2}\lambda + \frac{1}{2}(\nu - \mu - 1))}{\Gamma(\frac{1}{2}(\nu + 3 + \mu) - \frac{1}{2}\lambda)} 2^{\lambda-2\mu-4} \times \\ {}_2F_3\left(\frac{3}{2}, \frac{1}{2}(\mu + 1), \frac{1}{2}\mu + 1, \frac{1}{2}(3 + \mu - \nu) - \frac{1}{2}\lambda, \frac{1}{2}(3 + \mu + \nu) - \frac{1}{2}\lambda, -\frac{1}{4}k^4\right), \quad (2'3)$$

where  $R(2\mu - \lambda + 1) > 0$  and  $R(\nu) > -\frac{1}{2}$

Since as  $x \rightarrow \infty$ ,  ${}_1F_2(a; b, c, -\frac{1}{4}x^2) \sim O[x^{a-b-c+\frac{1}{2}} \cos(x+B) + Cx^{-2a}]$  and

$$|D_{\nu}(x)| \sim O[x^{\nu} e^{-\frac{1}{2}x^2}]$$

the left-hand side integral  $I_1$  is convergent if

$$R(2\mu - \lambda + 1) > 0, R(\lambda + 2\nu) > 0 \text{ and } R(\mu - 2\nu) < 2.$$

Hence by the theory of analytic continuation (2'3) holds if

$$R(\mu + \frac{1}{2}) > R(\frac{1}{2}\lambda) > R(-\nu) \text{ and } 2 > R(\mu - \nu) < R(\lambda).$$

*Interesting special cases of (2'3)*

(i) Two of the hypergeometric functions in (2'3) vanish and the other two reduce to single terms for  $\mu = 0$ , and we then obtain the integral

\*G. N. Watson Bessel Functions (Camb Univ Press, 1922), p. 436. This treatise will henceforth be referred to as B. F.

$$\int_0^{\infty} x^{-\lambda} D_{-\nu-\frac{1}{2}}(xe^{\frac{1}{2}\tau}) D_{-\nu-\frac{1}{2}}(\tau e^{-\frac{1}{2}\tau}) d\tau$$

$$= \frac{\Gamma(1-\lambda) \Gamma(\frac{1}{2}\lambda + \frac{1}{2}\nu) \sqrt{\pi}}{\Gamma(\nu + \frac{1}{2}) \Gamma(\frac{1}{2}\nu + 1 - \frac{1}{2}\lambda)} 2^{\lambda-2} \quad 1 > \text{Re}(\lambda) > -2\text{Re}(\nu)$$

(ii) The right side of (2.3) is also expressible in terms of Bessel functions under the circumstances  $\mu=1$  and  $\lambda = \nu+2$ . We then have

$$\int_0^{\infty} x^{2m} D_{m-\frac{1}{2}}(xe^{\frac{1}{2}\tau}) D_{m-\frac{1}{2}}(\tau e^{-\frac{1}{2}\tau}) {}_1F_2(1, 1+m-\frac{1}{2}+m, -\frac{1}{4}\tau^2) d\tau$$

$$= \frac{\Gamma(1+2m) \sqrt{\pi}}{\Gamma(\frac{1}{2}-m) 2^{1-2m}} \left[ \frac{\Gamma(2m) \Gamma(1-m)}{\Gamma(1-m) k^{4m}} {}_0F_1(1-m, -\tau^2/k^4) \right.$$

$$\left. + \frac{\Gamma(-m)}{2^{4m+1}} {}_0F_1\left(1+m-\frac{1}{4}\right) - \frac{\Gamma(-\frac{1}{2}-m) \tau^2}{\sqrt{\pi} 2^{4m+3}} {}_1F_2\left(1-\frac{1}{2}-m, -\frac{1}{4}\tau^2/k^4\right) \right]$$

$$= \frac{1}{2} \sqrt{\pi} \Gamma(m+1) \Gamma(2m+1) I^{-2m} \{H_{-1/2}(\tau^2) - Y_m(\frac{1}{2}\tau^2)\} \quad \frac{1}{2} > \text{Re}(m) > -\frac{1}{2}$$

where  $H_m(x)$  denotes Struve's Function and  $Y_m(\tau)$  Bessel function of the second kind

*Result 2* Applying the theorem to the operational relation (2.1) and\*

$$p J_p(\sqrt{2p}) K_p(\sqrt{2p}) = \frac{1}{2x} J_p\left(\frac{1}{x}\right) \quad \dots (3.1)$$

we are led to the integral

$$\int_0^{\infty} x^{2\mu-\lambda} J_{\nu}(\sqrt{x}) K_{\nu}(\sqrt{2x}) {}_1F_2(\mu, \mu + \frac{1-\lambda}{2}, \mu+1-\frac{1}{2}\lambda, -\frac{1}{4}x^2) dx$$

$$= \frac{1}{2} \Gamma(2\mu-\lambda+1) \int_0^{\infty} \frac{x^{\lambda-2}}{(x^2+k^2)^{\mu}} J_{\nu}\left(\frac{1}{x}\right) dx$$

$$= \frac{\Gamma(\rho+\frac{1}{2}\nu) \Gamma(\frac{1}{2}(\lambda-\nu+1)) \Gamma(2\rho)}{\Gamma(\mu) \Gamma(\nu+1) 2^{\nu+2} k^{\nu+2\rho}} {}_1F_2(\rho+\frac{1}{2}\nu, \nu+1-\frac{1}{2}(\nu+3-\lambda), \frac{1}{4k^2})$$

$$+ \frac{\Gamma(\frac{1}{2}(\nu-\lambda+1)) \Gamma(\rho)}{\Gamma(\frac{1}{2}(\nu+\lambda+1) 2^{\lambda+1} / 2^{\mu}} {}_1F_2(\mu, \frac{1}{2}(\nu+\lambda+1)-\frac{1}{2}(\lambda+1-\nu), \frac{1}{4k^2})$$

on putting  $2\mu-\lambda+1=2\rho$  and using a known formula† to evaluate the latter integral. The result is valid for  $0 < \text{Re}(\frac{1}{2}\mu-\frac{1}{2}\lambda+1) > \text{Re}(-\nu)$  and  $\text{Re}(\lambda) > -\frac{1}{2}$

\*S. C. Mitra, Bulletin Calcutta Math. Soc. 25, 1933, pp. 81-96

†B. F. p. 484

The hypergeometric function in the integrand reduces to a Bessel function if  $\lambda=1$  or  $\lambda=2$ , and we then obtain the integrals

$$\begin{aligned} & \int_0^{\infty} x^{\mu-\frac{1}{2}} J_{\nu}(\sqrt{2x}) K_{\nu}(\sqrt{2x}) J_{\mu-\frac{1}{2}}(\lambda x) dx \\ &= \frac{(4\lambda)^{-\mu-\frac{1}{2}}}{8\sqrt{\pi\nu}} \left[ \frac{\Gamma(\mu+\frac{1}{2}\nu)\Gamma(-\frac{1}{2}\nu)}{2\Gamma(\nu)(2\lambda)^{\nu}} {}_1F_2\left(\begin{matrix} \mu+\frac{1}{2}\nu; \\ 1+\frac{1}{2}\nu, 1+\nu, 4\lambda^2 \end{matrix}\right) \right. \\ & \quad \left. + \Gamma(\mu) {}_1F_2\left(\begin{matrix} \mu, \\ 1+\frac{1}{2}\nu, 1-\frac{1}{2}\nu, 4\lambda^2 \end{matrix}\right) \right] \end{aligned}$$

\*valid when  $R(\nu) < 2R(\mu) < 0$  and

$$\begin{aligned} & \int_0^{\infty} x^{\mu-\frac{1}{2}} J_{\nu}(\sqrt{2x}) K_{\nu}(\sqrt{2x}) J_{\mu-\frac{1}{2}}(\lambda x) dx \\ &= \frac{2^{\frac{1}{2}\mu}}{\sqrt{\pi}} \left[ \frac{\Gamma(\mu-\frac{1}{2}+\frac{1}{2}\nu)\Gamma(\frac{1}{2}-\frac{1}{2}\nu)}{4\Gamma(\nu+1)(2\lambda)^{\mu+\nu+\frac{1}{2}}} {}_1F_2\left(\begin{matrix} \mu-\frac{1}{2}+\frac{1}{2}\nu, \\ \nu+1, \frac{1}{2}\nu+\frac{1}{2}, 4\lambda^2 \end{matrix}\right) \right. \\ & \quad \left. + \frac{\Gamma(\mu)}{(\nu^2-1)(2\lambda)^{\mu+1}} {}_1F_2\left(\begin{matrix} \mu, \\ \frac{3+\nu}{2}, \frac{3-\nu}{2}, 4\lambda^2 \end{matrix}\right) \right] \end{aligned}$$

valid when  $0 > R(1-2\mu) < R(\nu)$  The former was given by Mitra\* for the case  $\mu=\frac{1}{2}$

Result 3 Taking the operational relations†

$$\frac{1}{x} \exp\left(-\frac{1}{x}\right) I_{\nu}\left(\frac{1}{x}\right) = 2p K_{\nu}(\sqrt{2p}) L_{\nu}(\sqrt{2p}), R(\nu) > -1, \quad (4.1)$$

and†

$$p^{k+1} \exp\left(\frac{1}{2p}\right) W_{k,m}\left(\frac{1}{p}\right) = \frac{2K_{k,m}(\sqrt{2x})x^{-k-\frac{1}{2}}}{\Gamma(\frac{1}{2}+m-k)\Gamma(\frac{1}{2}-m-k)}, R(\frac{1}{2} \pm m-k) > 0$$

an application of the theorem furnishes us with the integral

$$\begin{aligned} I_4 &\equiv \int_0^{\infty} I_{\nu}(\sqrt{2x}) K_{\nu}(\sqrt{2x}) K_{k,m}(2\sqrt{x}) x^{-k-\frac{1}{2}} dx \\ &= \frac{1}{2} \Gamma(\frac{1}{2}+m-k) \Gamma(\frac{1}{2}-m-k) \int_0^{\infty} x^{k-\frac{1}{2}} W_{k,m}\left(\frac{1}{x}\right) \exp\left(-\frac{1}{2x}\right) I_{\nu}\left(\frac{1}{x}\right) dx \\ &= \frac{\Gamma(\frac{1}{2}+m-k)\Gamma(\frac{1}{2}-m-k)}{\Gamma(\nu+1)2^{\nu+\frac{1}{2}}} \int_0^{\infty} x^{\nu-k-\frac{1}{2}} W_{k,m}(x) \exp(-\frac{1}{2}x) {}_0F_1(\nu+1, \frac{1}{2}x^2) dx \end{aligned}$$

\* S. C. Mitra *ibid*

† C. S. Meijer Proc Royal Acad, Amsterdam, 37 (1934), p. 805 See result (8).

on changing the variable and expressing  $I_\nu(x)$  in terms of the hypergeometric function  ${}_0F_1$

On using the equivalent infinite series for the function  ${}_0F_1$  and integrating term-by-term by the help of the formula\*

$$\int_0^\infty x^{l-1} e^{-\lambda x} W_{\kappa, m}(x) dx = \frac{\Gamma(l+m+\frac{1}{2})\Gamma(l-m+\frac{1}{2})}{\Gamma(l-k+1)}, \quad \operatorname{Re}(l+m+\frac{1}{2}) > 0$$

$$\begin{aligned} \text{we have finally} \quad & \int_0^\infty I_\nu(x) K_\nu(x) K_m(x \sqrt{2}) x^{-\frac{1}{2}} dx \\ &= \frac{\Gamma(\nu-k+m+\frac{1}{2})\Gamma(\nu-k-m-\frac{1}{2})\Gamma(\frac{1}{2}+m-k)\Gamma(\frac{1}{2}-m-k)}{\Gamma(\nu-2k+1)\Gamma(\nu+1)2^{\nu+\frac{1}{2}k+\frac{1}{2}}} \times \\ & {}_4F_1\left(\begin{matrix} \frac{1}{2}(\nu-k+m+\frac{1}{2}), \frac{1}{2}(\nu-k+m+\frac{1}{2}), \frac{1}{2}(\nu-k-m-\frac{1}{2}), \frac{1}{2}(\nu-k-m-\frac{1}{2}), 1 \\ \nu+1, \frac{1}{2}\nu-k+\frac{1}{2}, \frac{1}{2}\nu-k+1, \end{matrix}\right) \quad (4.2) \end{aligned}$$

provided that  $\operatorname{Re}(\nu-l \pm m) > -\frac{1}{2} < \operatorname{Re}(-k \pm m)$

The term-by-term integration effected in (4.2) is justified since  ${}_0F_1$  when expanded, is an infinite series of positive and continuous terms and being an integral function is uniformly convergent in the arbitrary interval  $(0, \alpha)$ , where  $\alpha$  may be taken as large as we please, and further  $x^{\nu-k-1} W_{\kappa, m}(x) e^{-\frac{1}{2}x}$  is bounded and integrable in  $(0, \alpha)$  and the integral in (4.2) converges under the conditions stated

*Result 1* Take again the relation (4.1) and the following†

$$W_{-\frac{1}{2}m, \frac{1}{2}m}\left(\frac{1}{p}\right) \exp\left(\frac{1}{2p}\right) p^{\frac{1}{2}(1-3m)} = \frac{2}{\Gamma(m+\frac{1}{2})} x^m K_m(\sqrt{x}) I_m(\sqrt{x}), \quad \operatorname{Re}(m) > -\frac{1}{2}$$

On proceeding exactly as in the preceding case it is found that

$$\begin{aligned} \int_0^\infty x^m K_m(\sqrt{x}) I_m(\sqrt{x}) K_\nu(\sqrt{2x}) I_\nu(\sqrt{2x}) dx &= \frac{\Gamma(m+\frac{1}{2})\Gamma(\nu+2m+1)\Gamma(\nu+m+1)}{\Gamma(\nu+1)\Gamma(\nu+2m+\frac{1}{2})2^{\nu+\frac{1}{2}}} \times \\ & {}_4F_3\left(\begin{matrix} m+\frac{1}{2}(\nu+1), \frac{1}{2}\nu+1+m, \frac{1}{2}(\nu+m+1), 1+\frac{1}{2}(\nu+m), 1 \\ \nu+1, m+\frac{1}{2}\nu+\frac{1}{2}, m+\frac{1}{2}\nu+\frac{1}{2}, \end{matrix}\right) \end{aligned}$$

provided that  $\operatorname{Re}(m+\nu+1) > 0 > \operatorname{Re}(m) > -\frac{1}{2}$  •

\* S. Goldstein, Proc. Lond. Math. Soc. (2), 34 (1952), pp. 106–125

† A. Erdelyi, Math. Zeit. 42 (1953), p. 131. This result can be deduced from the result (21)



The termwise integration required in the procedure also is easily justified as above

*Result 5.* Take now the relation (3.1) and the following\*

$$\frac{p^{2\mu-2m}}{(1+\lambda p)^{2\mu+1}} = \frac{\lambda^{m-2\mu}}{\Gamma(2m+2)} x^m \exp\left(-\frac{x}{\lambda}\right) M_{2\mu-m, m+1}\left(\frac{x}{\lambda}\right), \quad R(m) > -1.$$

Applying the theorem we have

$$\begin{aligned} I_7 &= \int_0^\infty J_\nu(\sqrt{2x}) K_\nu(\sqrt{2x}) x^m \exp\left(-\frac{x}{\lambda}\right) M_{2\mu-m, m+1}\left(\frac{x}{\lambda}\right) dx \\ &= \frac{\Gamma(2\mu-\nu+2\rho)}{\lambda k^{m-2\mu}} \int_0^\infty \frac{x^{\nu-2\rho}}{(1+\lambda x)^{1+2\mu}} J_\nu\left(\frac{1}{x}\right) dx. \end{aligned}$$

On putting  $x=1/t$  in the latter integral and using a known formula† to evaluate it, we find that

$$\begin{aligned} I_7 &= \frac{\Gamma(2\mu+2\rho-\nu)}{2^{\nu+1} \lambda^{\rho-\mu-\frac{1}{2}} \pi^{-1}} \left[ \frac{\Gamma(2\rho+2\mu)}{\Gamma(1+\nu)} \frac{\Gamma(1-2\rho)}{\Gamma(1+2\mu)} \lambda^{2\rho-1} {}_2F_3\left(\begin{matrix} \rho+\mu, \rho+\mu+\frac{1}{2} \\ \nu+1, \rho, \rho+\frac{1}{2} \end{matrix}; -\frac{1}{\lambda}\right) \right. \\ &\quad \left. + \frac{\Gamma(\rho-\frac{1}{2}) 2^{2\rho-2}}{\Gamma(\nu-\rho+\frac{3}{2})} {}_2F_3\left(\begin{matrix} \frac{1}{2}+\mu, 1+\mu \\ \frac{1}{2}, \frac{1}{2}-\rho, \frac{3}{2}+\nu-\rho \end{matrix}; -\frac{1}{\lambda}\right) - \right. \\ &\quad \left. \frac{(2\mu+1)\Gamma(\rho-1)}{\Gamma(\nu-\rho+2)} \lambda^{2\rho-3} \times {}_2F_3\left(\begin{matrix} 1+\mu, \frac{1}{2}+\mu \\ \frac{3}{2}, \nu+2-\rho, 2-\rho \end{matrix}; -\frac{1}{\lambda}\right) \right] \end{aligned}$$

provided that  $0 < R(\mu+\rho) > \frac{1}{2} R(\nu) < R(\rho) - \frac{1}{2}$

The  ${}_2F_3$  functions combine to give Bessel functions for  $\mu=0$  and  $\rho=\nu+\frac{1}{2}$ ; and we then have

$$\begin{aligned} &\int_0^\infty J_{\nu}(\sqrt{2x}) K_{\nu}(\sqrt{2x}) x^{\nu-1} \exp\left(-\frac{x}{\lambda}\right) M_{\frac{1}{2}-\nu, \frac{1}{2}}\left(\frac{x}{\lambda}\right) dx \\ &= \frac{1}{2} \pi \sec \pi \nu \Gamma(\nu+1) \lambda^{\frac{1}{2}(\nu+1)} \{H_{-\nu}(k) - Y_{-\nu}(k)\}, \quad -\frac{1}{2} < R(\nu) < \frac{3}{2} \end{aligned}$$

\* A Erdelyi, Proc. Koninklijke Nederlandsche Akad. van Wetenschappen, 41, 5, (1938). See his relation (14)

*Result 6.* By term-by-term interpretation it is easy to see that

$$\begin{aligned} I_\nu \left( \frac{x}{a} \right) \exp \left( -\frac{x}{a} \right) &= \frac{1}{\Gamma(1+\nu)} \left( \frac{x}{2a} \right)^\nu {}_1F_1 \left( \nu + \frac{1}{2}, 2\nu + 1, -\frac{2x}{a} \right) \\ &= \left( \frac{1}{2ap} \right)^\nu {}_2F_1 \left( \nu + \frac{1}{2}, \nu + 1, -\frac{2}{ap} \right) \\ &= (1 + 2/ap)^{-\frac{1}{2}} (\sqrt{1 + \frac{1}{2}ap} - \sqrt{\frac{1}{2}ap})^{2\nu}, a > 0 \end{aligned}$$

Applying the theorem to this relation and (31), we are furnished with the integral

$$\begin{aligned} &\int_0^\infty \frac{(\sqrt{1 + \frac{1}{2}ax} - \sqrt{\frac{1}{2}ax})^{2\nu}}{\sqrt{\{(ax+2)x^2\}}} J_\nu \left( \frac{1}{x} \right) dx \\ &= \frac{2}{\sqrt{a}} \int_0^\infty J_\nu (\sqrt{2x}) K_\nu (\sqrt{2x}) I_\nu \left( \frac{x}{a} \right) \exp \left( -\frac{x}{a} \right) dx \\ &= \frac{\Gamma(\nu + \frac{1}{2})}{\sqrt{\pi}} D_{-\nu-\frac{1}{2}} (\sqrt{ae^{i\pi}}) D_{-\nu-\frac{1}{2}} (\sqrt{ae^{-i\pi}}), \operatorname{Re}(\nu) > -\frac{1}{2}, a > 0 \end{aligned}$$

where I have used for the latter equality a result obtained by me elsewhere



# PROCEEDINGS

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### THE PARTIAL PRESSURES OF ATOMS AND MOLECULES IN THE SATURATED VAPOURS OF THE ALKALI ELEMENTS

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In determining experimentally the vapour pressures of the alkali metals it is generally assumed that the vapours consist entirely of monatomic molecules. This assumption renders the calculation of the vapour pressures from the observational data particularly simple, and the results obtained are sufficiently accurate for most purposes. But occasionally one needs the values for the partial pressures of the monatomic and diatomic molecules separately, in the saturated vapour. Though the observational data available are sufficient to enable us to calculate from them these partial pressures, the calculation involved is laborious. Further, the details of the calculation differ according to the method used in obtaining the original experimental data, because when we take into account the presence of the diatomic molecules also in the vapour, it is found that the data obtained by the different methods do not refer to the same physical quantity. For example, the static method gives the sum of the partial pressures of the monatomic and the diatomic vapours, whereas the effusion and the gas flow methods do not give directly either the total or the partial pressures. To the order of approximation aimed here the presence of the different isotopes also have to be taken into account, particularly in the case of light atoms like lithium.

In the present paper are deduced formulae for calculating the partial vapour pressures of the monatomic and diatomic components of the vapour, from the data obtained by different experimental methods. Values are given for the partial pressures for lithium, sodium and potassium for a wide range of temperatures. Sufficient data are not available to enable us to make similar calculations for the other alkali metals, rubidium and caesium.

## 1 INTRODUCTION

Ladenburg and Thiele (1929) were the first to take into account the presence of diatomic molecules in the vapours of the alkali elements and they gave formulae

for obtaining the partial pressures of monatomic and diatomic molecules from the values of the vapour pressure determined in the usual manner by the effusion method and by the gas flow method. Their formula in the case of the effusion method, however, appears to be incorrect

L. C. Lewis (1931) measured  $\alpha$ , the ratio of the partial pressures of the diatomic and monatomic molecules in the vapour, by determining the relative intensities of the split and the unsplit beams when a beam of the vapour is passed through an inhomogeneous magnetic field. From this he calculated the equilibrium constant for the reaction  $2A \rightleftharpoons A_2$ , and the heats of dissociation in the case of sodium, potassium and lithium. Later Thiele (1932), using Lewis's values for the heat of dissociation, calculated the partial pressures of the monatomic and diatomic molecules from his own observations obtained by the gas flow method. He also calculated the partial pressures from the observations of Edmondson and Egerton (1927) made by the effusion method. In the latter calculations Thiele used the same formula as given earlier by Ladenburg and Thiele

Bogros (1932) considered the presence of isotopes in lithium vapour, but he did not take into account the presence of diatomic molecules

In the present paper general formulæ have been worked out to obtain the partial pressures of the monatomic vapours of the different isotopes, and of the diatomic vapour, from the experimental data obtained by different methods. Using these formulæ calculations have been made of the partial pressures of the monatomic and the diatomic molecules in the saturated vapours of sodium, potassium and lithium at different temperatures. Similar calculations could not be made for the other two alkali elements, rubidium and caesium, since their rotational and vibrational constants are not known, without which  $\alpha$  cannot be calculated. Graphs have been plotted from which partial pressures at any temperature can be found out.

## 2. FORMULÆ FOR THE CALCULATION OF THE PARTIAL PRESSURES

Ditchburn and Gilmour (1941) have given a survey of the various experimental methods for the determination of the vapour pressures of metals. Most of the low pressure data have, however, been obtained by the effusion method, the gas flow method and the statical method and so we confine ourselves to these methods.

*The effusion method*—In this method the vapour effusing out through a hole of known area in a certain time is condensed, and its amount estimated, usually by titration. If  $n$  is the number per c. c., of particles of mass  $m$ , in the vapour, then the number effusing out per sec. through unit area of the hole is

$$i = \frac{1}{4} n \bar{v} = \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}}$$

But  $p = nkT$ ,

Therefore  $p = v\sqrt{2\pi mkT}$

Now, if all the particles are not of the same mass, i.e., if there are isotopes and diatomic molecules in the vapour, their rates of effusion will be different. Let  $n_1, n_2$  be the numbers of molecules of the isotopes ( $n_1$  being more abundant) and  $n_{11}$  the number of diatomic molecules, all per c.c., and  $m_1, m_2$  and  $m_{11}$  respectively their masses. Then the numbers of each effusing in unit time through unit area of the hole will be given by

$$\begin{aligned}v_1 &= n_1 \sqrt{\frac{kT}{2\pi m_1}} = A \frac{n_1}{\sqrt{m_1}} \\v_2 &= n_2 \sqrt{\frac{kT}{2\pi m_2}} = A \frac{n_2}{\sqrt{m_2}} \\v_{11} &= n_{11} \sqrt{\frac{kT}{2\pi m_{11}}} = A \frac{n_{11}}{\sqrt{m_{11}}},\end{aligned}$$

where  $A = \sqrt{\frac{kT}{2\pi}}$

(The number of molecules in which the less abundant isotope occurs is taken to be negligible.) Therefore the number of atoms contained in the effused matter, as obtained by titration, is

$$v = v_1 + v_2 + 2v_{11} = A \left( \frac{n_1}{\sqrt{m_1}} + \frac{n_2}{\sqrt{m_2}} + \frac{2n_{11}}{\sqrt{m_{11}}} \right) \quad (1)$$

Let  $\frac{n_2}{n_1} = \alpha$  and  $\frac{n_{11}}{n_1} = \varepsilon$ . Then  $n = n_1 + n_2 + n_{11} = n_1(1 + \alpha + \varepsilon)$

Hence we have from (1)

$$\begin{aligned}v &= A \cdot n_1 \left( \frac{1}{\sqrt{m_1}} + \frac{\alpha}{\sqrt{m_2}} + \frac{2\varepsilon}{\sqrt{m_{11}}} \right) \\&= \sqrt{\frac{kT}{2\pi}} \frac{n}{1 + \alpha + \varepsilon} \left( \frac{1}{\sqrt{m_1}} + \frac{\alpha}{\sqrt{m_2}} + \frac{2\varepsilon}{\sqrt{m_{11}}} \right), \quad (2)\end{aligned}$$

and  $p = nkT = v \cdot \frac{1 + \alpha + \varepsilon}{\frac{1}{\sqrt{m_1}} + \frac{\alpha}{\sqrt{m_2}} + \frac{2\varepsilon}{\sqrt{m_{11}}}} \sqrt{2\pi kT} \quad (3)$

This is the general formula for the total pressure of a vapour in the case of effusion method. From this the partial pressures  $p_1, p_2$  and  $p_{11}$  can be calculated since

$$p_1 = \frac{p}{1 + \alpha + \varepsilon}, \quad p_2 = \alpha p_1, \quad \text{and} \quad p_{11} = \varepsilon p_1 \quad (3A)$$

Edmondson and Egerton's calculations assume that both  $\alpha$  and  $\varepsilon$  are zero. Hence the values of pressure as given by them are

$$p_{EE} = \nu \sqrt{m_1} \sqrt{2\pi kT} \quad . \quad . \quad . \quad (4)$$

We can calculate the correct pressure from the values of the pressure given by Edmondson and Egerton by a combination of (3) and (4) Hence

$$p = \frac{p_{EE}}{\sqrt{m_1}} \frac{1 + \alpha + \varepsilon}{\sqrt{\frac{1}{m_1}} + \sqrt{\frac{\alpha}{m_2}} + \sqrt{\frac{2\varepsilon}{m_{11}}}} \quad (5)$$

Bogros considers  $\varepsilon = 0$  Hence

$$p_B = \nu \frac{1 + \alpha}{\sqrt{\frac{1}{m_1}} + \sqrt{\frac{\alpha}{m_2}}} \sqrt{2\pi kT} \quad . \quad . \quad . \quad (5A)$$

By a combination of (3) and (5A) we get the correct pressure from the values of pressure given by Bogros. Hence

$$p = p_B \frac{\frac{1}{\sqrt{m_1}} + \frac{\alpha}{\sqrt{m_2}}}{1 + \alpha} \frac{1 + \alpha + \varepsilon}{\frac{1}{\sqrt{m_1}} + \sqrt{\frac{\alpha}{m_2}} + \sqrt{\frac{2\varepsilon}{m_{11}}}} \quad . \quad . \quad . \quad (6)$$

Knowing the total pressure  $p$ , the partial pressures  $p_1$ ,  $p_2$  and  $p_{11}$  can be calculated by the help of (3A).

In making these calculations  $\alpha$  is assumed to be constant and its value is taken from the tables of relative abundance of isotopes  $\varepsilon \left( = \frac{p_{11}}{p_1} \right)$  is calculated for different temperatures from Gibson and Heitler's equation when the rotational and vibrational constants of the molecule are known.

$$\log K = \log \frac{v_{\text{atom}}^2}{p_{\text{mol}}} = - \frac{D}{4 \cdot 578T} + \frac{3}{2} \log \frac{\pi m k T}{h^2} - \log \frac{8\pi^2 I}{h^2} + \log \left( 1 - e^{-\frac{h\nu_0}{kT}} \right) + \log 2 + 2 \log g_{\text{atom}} \quad . \quad . \quad (7)$$

*Gas flow method.*—The experimental substance is contained in a chamber whose temperature can be adjusted. A stream of inert gas strikes the surface of the substance, becomes saturated with its vapour, and passes out. The vapour thus carried by the gas is condensed in a cool tube, and its amount estimated by titration. Let  $\nu_g$  be the number of gas molecules passing out in a certain time, and  $\nu$  the number of the molecules of vapour that pass out with the gas

The numbers of molecules per c.c. of the gas and of the vapour in the chamber must be proportional to the numbers  $\nu_g$  and  $\nu$  respectively that pass out. Hence we have

$$\begin{aligned} p &= C \nu k T \\ P &= C. (\nu + \nu_g) k T, \end{aligned}$$

where  $p$  is the partial pressure of the vapour in the chamber, and  $P$  is the total pressure, and  $C$  is a constant. Therefore,

$$p = \frac{\nu}{\nu + \nu_g} \cdot P \quad . \quad (8)$$

The number  $\nu$  of the vapour molecules is estimated by titration,  $\nu_g$  is found by the help of a gasometer, and  $P$  the total pressure is measured by a manometer. Thus  $p$  can be calculated. If, however, isotopes and diatomic molecules are present we have, working as before,

$$p = \nu_1 (1 + \alpha + \epsilon) C k T,$$

where  $\nu_1$  is the number of the monatomic molecules (more abundant) in the outgoing vapour of the metal, and hence

$$p = \frac{\nu_1 (1 + \alpha + \epsilon)}{\nu_1 (1 + \alpha + \epsilon) + \nu_g} P \quad . \quad (9)$$

In most of these experiments the quantity  $\nu$  occurring in (8) is measured by titration and, therefore, its value as determined in these experiments on the assumption of monatomicity is  $\nu_1 (1 + \alpha + 2\epsilon)$ . Hence from (8) the pressure  $p_0$  as recorded by these experimenters is given by

$$p_0 = \frac{\nu_1 (1 + \alpha + 2\epsilon)}{\nu_1 (1 + \alpha + 2\epsilon) + \nu_g} P \quad . \quad (10)$$

From (9) and (10) the correct pressure  $p$  is given by the relation

$$\begin{aligned} p &= p_0 \frac{1 + \alpha + \epsilon}{\nu_1 (1 + \alpha + \epsilon) + \nu_g} \times \frac{\nu_1 (1 + \alpha + 2\epsilon) + \nu_g}{1 + \alpha + 2\epsilon} \\ &= p_0 \frac{1 + \alpha + \epsilon}{1 + \alpha + 2\epsilon} \text{ approx.} \quad . \quad (11) \end{aligned}$$

In these experiments the pressure of the inert gas is about an atmosphere and the pressure of the vapour is about 2 to 3 mm. Consequently  $\nu_1 \epsilon \ll \nu_g$ . We have therefore

$$p_1 = \frac{p}{1 + \alpha + \epsilon} = \frac{p_0}{1 + \alpha + 2\epsilon} \quad . \quad (12)$$

and from this  $p_2$  and  $p_{11}$  can be calculated.



If  $\alpha=0$ , i.e., if the rarer isotopes are negligible,

$$p_1 = \frac{p_0}{1+\varepsilon}$$

which is the same formula as that given by Ladenburg and Thiele for the partial pressure of the monatomic molecules in the case of gas flow method.

*Statcal method.*—In this method the pressure of the vapour is measured directly and the observed pressure is, therefore the sum of the partial pressures. Hence, if  $p_1$ ,  $p_2$  and  $p_{11}$  denote the partial pressures of the two isotopes and the diatomic molecules respectively, as before, we have

$$\begin{aligned} p &= p_1 + p_2 + p_{11} \\ &= p_1 (1 + \alpha + \varepsilon), \end{aligned}$$

and therefore

$$p_1 = \frac{p}{1 + \alpha + \varepsilon} \quad (13)$$

### 3. VAPOUR PRESSURE VALUES

*Sodium*—The most accurate measurements on the vapour pressures of sodium are those of Rodebush and de Vries (1925) and Edmondson and Egerton (1927) both made by Knudsen's effusion method, and those of Thiele (1932) made by the gas flow method Thiele's values are for a higher range of temperature, and from these values he has calculated the partial pressure of the monatomic molecules of sodium in the vapour

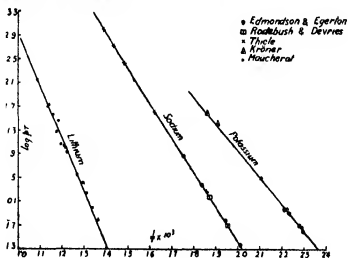


Fig 1

The vapour pressure values at different temperatures given by these workers for sodium were all plotted on a single graph in which  $\log pT$  represents the

ordinate and  $\frac{1}{T}$  the abscissa (Fig. 1). It was found that all of them plotted well on a straight line, passing through the known boiling point of sodium at atmospheric pressure, and having a slope which agreed well with the known latent heat of evaporation  $\lambda_0 = 26.2 \text{ K cal}$ , thus verifying the inter-consistency of these values.

Adopting these values, the partial pressures of the monatomic and diatomic molecules in the saturated vapour of sodium at different temperatures were calculated with the help of relations (5) or (12) as the case might be, and (3A). In this calculation  $\alpha$  was taken to be zero, i.e., isotopes of sodium other than  $\text{Na}_{23}$  were taken to be negligibly small.

The values of  $\epsilon$  at different temperatures required in these calculations were obtained from equation (7) using the known values of  $D$ ,  $\omega_0$  and  $I$ , and the approximate value for  $p_1$ . The values adopted for the other constants were  $D = 16.8 \text{ K cal}$ ;  $B = 0.154 \text{ cm}^{-1}$ ,  $\omega_0 = 158.5 \text{ cm}^{-1}$ .

The calculated values of the partial pressures  $p_1$  and  $p_{11}$  are plotted in Fig. 2. Following Thiele we have plotted  $\log p_1 T$  and  $\log p_{11}$  respectively against  $1/T$ . Both give smooth straight lines.

The partial pressures  $p_1$  and  $p_{11}$  at any desired temperature can be read off from these graphs.

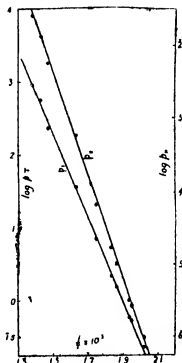


Fig. 2

*Potassium*—Comparatively little work has been done on the vapour pressure of potassium. The results of Hackspill (1913) are approximate only. In our calculation the following values have been adopted as being the most accurate. Those of Kroner (1913), who employed a modified statical method, and measured with the aid of a Rayleigh differential manometer the volume change, at constant pressure of nitrogen, that occurred when the metal was vaporized. His values extend over the range  $250^{\circ}$ – $400^{\circ}\text{C}$ . (2) Those of Edmondson and Egerton (1927) who employed Knudsen's method and have obtained the vapour pressure in the range  $100^{\circ}$ – $200^{\circ}\text{C}$ . The values of Kroner and those of Edmondson and Egerton when plotted, are found to lie on a single line, as in the case of sodium, and these values have been adopted for our calculations.

The calculated values of the partial pressures  $p_1$  and  $p_{11}$  are plotted in Fig. 3. The values adopted for the constants were  $D=14.5 \text{ K cal}$ ,  $B=0.056 \text{ cm}^{-1}$ ,  $\omega_0=92.64 \text{ cm}^{-1}$ .  $p_2$  can be obtained from  $p_1$  from the known value of  $\alpha$ , namely, 0.07.

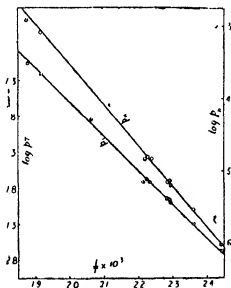


Fig 3

*Lithium*—The earliest work on the vapour pressure of lithium is that of Hartmann and Schneider (1929). When a line is drawn through their high pressure points it passes tolerably well through the low pressure points of Bogros (1932) and Maucherat (1939) also. In the following calculations Maucherat's values have been adopted, as the straight line drawn through his observations yields for the boiling point the value  $1400^{\circ}\text{C}$ , which is in agreement with that

given by Ruff and Johnsen (1905) and for  $\lambda_0$  a value well in agreement with the value 36410 cal given by Fischer and Kelley (1935). Since the points of Maucherat are widely scattered the values adopted in our calculations are those directly obtained from the graph. From these values the partial pressures are calculated with the help of relations (6) and (34). The results are plotted in Fig. 4.

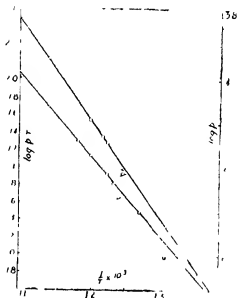


Fig. 4

It will be seen from the graphs that the ratio of the diatomic to the monoatomic molecules is very small at low temperatures but gradually *increases* with rise of temperature. This increase with temperature may appear at first sight somewhat strange, but it can be seen to be the direct consequence of the law of mass action and the large increase in the atomic vapour pressures with rise of temperature.

My sincere thanks are due to Dr. B. N. Srivastava under whose guidance this work has been carried out.

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# THE THERMAL IONIZATION OF SODIUM AND POTASSIUM ATOMS

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An account is given of measurements on the thermal ionization of sodium and potassium atoms. The vapours of these substances enter a vacuum graphite furnace where they suffer thermal ionization. The products of the ionization, namely, the ionized atoms and electrons, effuse out through a narrow opening, and are separately collected and measured. From these measurements their respective concentrations inside the furnace are calculated, and thence the ionization constant and the energy of ionization. The energy of ionization is found to be 118.5 K cal for the sodium atom and 99.9 K cal for the potassium atom.

## 1. INTRODUCTION

The thermal ionization of atoms has been studied experimentally by several workers. The ingenious method developed by Langmuir and Kingdon (1925) and used by them for the study of the thermal ionization of caesium vapour has been adopted by many workers, e.g. by Killian (1936) for rubidium, by Meyer (1930) for potassium, and by Morgulis (1934) for sodium. This method, however, involves uncertainties due to the adsorption of the atoms and ions on the surface of the filament. The thickness of this adsorbed layer is found to vary with the temperature of the filament and with the pressure of the vapour, and is not uniform all over the filament surface.

The adsorbed layer alters the thermionic work function and thereby considerably changes the intensity of electronic emission. Hence the uncertainties referred to. On the other hand the method developed by Srivastava (1940a) is direct and simple. It is based on the measurement of the rate of effusion of the products of thermal ionization from inside a heated chamber containing the vapour through a tiny hole in the side of the chamber. Using this method, and using a vacuum furnace for the production of the required high temperatures, Srivastava investigated experimentally the thermal ionization of barium and strontium up to about 1600°C. The results obtained were found to be in good agreement with the theory.

In the present paper the same method has been employed to study the thermal ionizations of sodium and potassium atoms. The temperatures used are

higher than those used by Srivastava for barium and strontium, and extend up to  $1700^{\circ}\text{C}$ . The high reactivity of sodium and potassium requires care in working. The ionization potential of potassium being low the ionic currents involved are much larger than in barium or strontium, or even in sodium, and one can therefore work with smaller angular apertures for the collecting Faraday cylinder—which is an advantage.

## 2. APPARATUS

A full description of the apparatus has been given by Srivastava in his paper on barium.

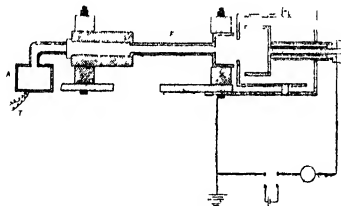


Fig. 1—Vacuum-graphite furnace

Briefly the main furnace consists of a graphite tube 'F' (Fig. 1) bound to electrodes inside a vacuum chamber. The tube is heated by the passage of a heavy current through it from a low tension transformer. Since for sodium and potassium much lower temperatures are required to develop the necessary vapour pressure, the auxiliary furnace 'A', containing the metal, was screwed on to the end of the main graphite furnace and was made of iron. The auxiliary furnace is heated by conduction from the main furnace and the length of the tube connecting the two was adjusted so as to provide the requisite temperature in the auxiliary furnace, which was read by the thermocouple 'T'.

## 3. THEORY OF THE METHOD

From a consideration of the geometry of the arrangement of the graphite furnace, namely, with the effusion hole at its end and the limiting diaphragm of the Faraday cylinder placed at some distance, Srivastava (1938) has shown that the ionic current is given by

$$i_z^+ = \frac{ep_i S}{\sqrt{2\pi m_i k T}} \cdot \frac{r^2}{r^2 + d^2} \quad (1)$$

where  $p_i$  is the partial pressure of the ions inside the furnace  $m_i$  the mass of each ion,  $S$  the area of the effusion hole  $e$  the charge on an ion,  $r$  the radius of the limiting diaphragm and  $d$  is the distance of the limiting diaphragm from the effusion hole. Similarly, for the electronic current

$$i_K = \sqrt{\frac{e p_e S}{2\pi m_e kT}} \frac{r^2}{r^2 + d^2}, \quad (2)$$

where  $p_e$  denotes the partial pressure of the electrons in the main furnace and  $m_e$  the mass of an electron.

From (1) and (2) we have

$$K = \frac{p_i p_e}{p_a} = \frac{2\pi kT}{e^2 S^2} \left( \frac{r^2 + d^2}{r^2} \right)^2 \frac{i_K^4 i_g}{p_i} \sqrt{m_i m_e} \quad (3)$$

where  $p_a$  denotes the pressure of the un-ionized atoms in the main furnace.

If  $\epsilon$  is the sensitivity of the galvanometer and  $d^+$  and  $d^-$  are the deflections corresponding to  $i_K^+$  and  $i_K^-$  we have  $i_K^+ = \epsilon d^+$  and  $i_K^- = \epsilon d^-$  and substituting in (3) we obtain

$$K = \frac{2\pi kT}{e^2 S^2} \left( \frac{r^2 + d^2}{r^2} \right)^2 \epsilon^2 \frac{d^+ d^-}{p_a} \sqrt{m_i m_e} \quad (4)$$

where the pressures are expressed in atmospheres.

According to Darwin and Fowler's modification of the ionization formula we have

$$\ln \frac{p_i p_e}{p_a} = -\frac{\chi_1}{kT} + \frac{5}{2} \ln T + \ln g_e \frac{(2\pi m_e)^{3/2} h^{-5/2}}{h^3} - \ln b(T) + \ln b'(T) \quad (5)$$

where  $\chi_1$  is the energy required to ionize the unexcited atom and  $g_e$  the weight factor of the electron which is equal to 2. Now

$$b(T) = g_1 + g_2 e^{-(\chi_1 - \chi_2)/kT} + \dots + g_n e^{-(\chi_1 - \chi_n)/kT} + \dots \quad (6)$$

$$b'(T) = g_{1,1} + g_{1,2} e^{-(\chi_{1,1} - \chi_{1,2})/kT} + \dots + g_{n,n} e^{-(\chi_{n,1} - \chi_{n,n})/kT} + \dots \quad (7)$$

$g_n$  and  $g_{n,i}$  denote the weight factors and  $\chi_n$  and  $\chi_{n,i}$  the energies required to ionize the normal atom and the excited atom in the  $n$ th quantum state respectively. Eqn. (5) may be written

$$\log K = -\frac{U}{4.573T} + \frac{5}{2} \log T - 6.479 + \log 2 + \log b'(T) - \log b(T) \quad (8)$$

where  $U$  is the energy of ionization of a gram-atom of the metal in calories, and is equal to  $\frac{N_e V_i}{300J}$ , where  $V_i$  is the ionization potential of the metal. The pressures are all expressed in atmospheres.  $V_i$  for sodium is equal to 5.12 volts



and for potassium 4.32 volts.  $b(T)$  and  $b'(T)$  have been calculated from the energy states given by Bacher and Goudsmit (1932). For both sodium and potassium  $b(T)$  comes out to be 2.0002 and  $b'(T)$  1.0000 at the temperature of the experiment. Eq. (8) reduces to

$$\log K = -\frac{U}{4.573T} + \frac{5}{2} \log T - 6.479 \quad (9)$$

Substituting the experimentally determined value of  $K$  from (4) in (9)  $U$  can be calculated.

## 4. EXPERIMENTAL

The graphite tube furnace was thoroughly outgassed by sending a large intermittent heating current through the graphite tube till the charge collected in the Faraday cylinder in a blank experiment became negligible.\* The metal was then introduced in the auxiliary furnace. The heating current was varied to change the temperature of the main furnace. Corresponding to any one temperature of the furnace, the temperature of the auxiliary furnace was measured, the negative and positive current deflections of the galvanometer, for a given positive or negative potential applied to the Faraday cylinder were also observed. The currents are extremely sensitive to temperature fluctuations in the main furnace caused by slight variations in the supply voltage. Readings are taken only when the temperature is steady.

One of the quantities to be determined in eq. (3) is  $p_a$ . This is the partial pressure of the atoms in the main furnace. This can be approximately calculated from the relation

$$p_a = (p_A + p_M \sqrt{2}) \sqrt{\frac{T'}{T}} \quad (10)$$

as has been shown by Srivastava (1940). Here  $p_A$  and  $p_M$  refer to the partial pressures of the monatomic and the diatomic molecules respectively in the auxiliary furnace in which the metal is contained.  $T'$  and  $T$  are the temperatures of the main and the auxiliary furnaces respectively. The values of  $p_A$  and  $p_M$  in the saturated vapour of sodium and potassium at different temperatures have already been calculated by the author elsewhere (Bhatnagar, 1943) and the results

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\* Though the vapour pressure of the electrons inside the graphite chamber due to the evaporation of electrons from the surface of graphite is negligible in comparison with the vapour pressure of electrons due to the ionization of the sodium or the potassium atoms led into the chamber, the former pressure (namely of electrons in equilibrium with the graphite surface) can be measured and the work function of graphite calculated therefrom. This is dealt with in a separate paper which will be published soon in this Journal.

depicted in the form of graphs from which the values required at different temperatures in this experiment have been read

## 5. RESULTS

*Sodium*—Morgulis (1934) studied the thermal ionization of sodium vapour on a glowing tungsten surface. Later in the same year Dobazow (1934) investigated the ionization of sodium vapour on tungsten and molybdenum surfaces, and that of potassium on tungsten coated with thorium. Altman, Kerbe and Rompe (1934) have studied the ionization of sodium and caesium vapours on glowing tungsten and rhenium surfaces. The experimental method followed in all the above determinations was that of Langmuir and Kingdon. With sodium on tungsten surface Morgulis found little ionization at low temperatures but at high temperatures the sodium layer evaporates resulting in an increase of ionization. For a single temperature however he finds different degrees of ionization for different pressures which seems to be due to the varying adsorption of the atoms on the filament surface. The experiments can therefore be considered hardly satisfactory.

The observations on the thermal ionization of sodium, made by the present method, are given in Table I. As will be seen from the Table the results obtained are within 1.6% of the value of  $U$  as determined spectroscopically.

*Potassium*—The ionization of potassium on tungsten surface has been studied by M. J. Copley and T. J. Plupps (1935) and on glowing platinum and tungsten surfaces by H. Meyer (1937). These determinations also are subject to the same uncertainties as those of sodium.

The value of  $p_1$  for potassium has been determined in the same way as for sodium.

Table II gives the observations on the thermal ionization of potassium and the calculated value of  $U$ . It will be observed that the experimental value of  $U$  agrees with the value of 1 determined spectroscopically to within 1.8%.

TABLE I

## THERMAL IONIZATION OF SODIUM

Distance between the effusion hole and the limiting diaphragm = 17.5 mm  
 Diameter of the effusion hole = 0.928 mm Diameter of the limiting diaphragm = 8.4 mm  
 Potential applied to the cylinder = 4 volts Current sensitivity of the galvanometer =  $1.25 \times 10^{-8}$  amp/mm

Mean temp of graphite furnace in °C	Temp of auxiliary furnace in °K	Vap pres in aux fur in mm $p_{\text{aux}} \times 10^{-1}$	Vap pres in graphite fur- nace in mm $p \times 10^{-2}$	Negative deflection in mm $d$	Positive deflection in mm $d'$	$\log_e k$ [from eq (4)] + 10	L in K cal/s
1585	1565	7.161	3.30	1.317	40 × 100	18	2.7872
1595	1575	7.499	3.908	1.382	54 × 100	24	2.788
1600	1630	9.661	4.842	1.774	70 × 100	30	3.0761
1610	1600	12.4	6.33	2.28	71 × 100	30	3.078
1615	1620	13.84	7.328	2.900	90 × 100	30	3.1038
1620	1590	17.76	10.30	3.148	71 × 100	36	2.9171
1630	1610	18.60	11.30	3.809	77 × 100	44	3.184
1640	1640	20.84	13.09	3.814	81 × 100	40	3.254
1625	1650	10.30	3.809	1.910	62 × 100	30	3.0380
1632	680	11.80	6.166	2.194	88 × 100	40	3.368
1680	1775	16.20	14.41	3.007	43 × 300	60	3.5520
1685	1820	19.70	19.02	3.647	41 × 300	60	3.563
						Mean	118.9
						Spectroscopic value	118.0

**TABLE II**  
**THERMAL IONIZATION OF POTASSIUM**

Mean temp of graphite furnace in °C	Temp of aux. turnace in °K	Vap pres in aux furnace in mm		Vap pres in graph furnace in mm	Negative deflection in mm <i>d</i>	Positive deflection in mm <i>d'</i>	Log K from eq (4) +15	U in K cal
		$p_{atm} \times 10^4$	$p_{red} \times 10^5$					
1483	466	4.742	5.003	0.9356	51 × 100	24	4.0452	100.7
1503	471	5.984	7.063	1.188	97 × 100	50	4.5903	99.0
1540	472	6.281	7.499	1.254	120 × 100	60	4.7516	98.8
1545	474	6.823	8.370	1.360	128 × 100	70	4.7949	98.5
1555	475	7.178	8.913	1.432	46 × 300	90	4.8830	98.6
1591	484	10.72	15.14	2.145	78 × 300	47 × 3	5.1914	98.1
1630	489	13.21	19.95	2.660	111 × 300	70 × 3	5.4333	98.2
1536	472	6.295	7.499	1.252	113 × 100	54	4.6792	99.2
1541	473	6.607	8.035	1.317	45 × 300	60	4.7816	98.6
1546	475	7.178	8.913	1.429	45 × 300	66	4.8241	98.3
1606	482.5	9.908	13.74	1.996	51 × 300	40 × 3	4.9983	100.7
1620	484.5	10.76	15.31	2.171	54 × 300	140	5.0301	101.2
1575	477	8.072	10.35	1.615	57 × 300	42 × 3	5.0301	100.9
1596	485	11.14	15.85	2.230	68 × 300	59 × 3	5.2148	98.2
							Mean	99.9
							Spectroscopic value	99.5

## 6 DISCUSSION OF THE RESULTS

It will be observed that a small percentage error in the measurement of the temperature of the main furnace produces an error of the same order in  $U$ . Now 1% error in the mean temperature used in the calculation is very likely. The temperature distribution along the graphite furnace depends on the thickness of the tube. It is maximum over a small region in the middle and falls off at the ends. To get the mean temperature, the temperature over the whole length of the tube at short distances from the centre is measured up to the effusion hole and the mean obtained. This procedure, though not the best, is the only one available. This limits the degree of accuracy with which the temperature of the furnace can be determined though the pyrometer can measure temperatures correct to about  $2^{\circ}\text{C}$ . Hence the observed deviations in the value of  $U$  in our experiments with sodium and potassium are well within the limits of experimental error. The value of  $\log K$  is very much affected by any error in the measurement of the radius of the effusion hole as this quantity occurs in the fourth power in the equation. The hole is extremely small and is made as perfectly circular as possible. The diameter is then taken as the mean of twenty diameters.

In conclusion, I take this opportunity of expressing my sincere thanks to Dr B. N. Srivastava, D Sc, under whose guidance this work has been done, and to Dr A. N. Tandon for allowing me to use some observations made by him on sodium and potassium, and to the University of Allahabad for meeting the expenses of publication of this paper.

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# STRUCTURE OF LIQUID $\text{PCl}_3$

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The triangular bi-pyramid model and the square pyramid model for the molecule of liquid  $\text{PCl}_3$ , have been examined, and a normal co-ordinate treatment has been made to find the force-constants and frequencies in either case. The force-constants are obtained from the polarized Raman frequencies of the liquid spectrum. It is found that for the triangular bi-pyramid model the P-Cl force-constant in  $\text{PCl}_3$  has a greater value than that in  $\text{PCl}_5$ , although the P-Cl distance in  $\text{PCl}_3$  is greater than that in  $\text{PCl}_5$ . The Cl-Cl force-constant is negative although it is positive in other compounds. These considerations and those of dipole moments enable us to discard the triangular bi-pyramid model.

A fairly good agreement between the observed and calculated frequencies for the square pyramid model is obtained by assuming the P-Cl force-constant as  $1.5 \times 10^8$  dynes, Cl-Cl force-constant as  $3 \times 10^8$  dynes,  $d' = \frac{d}{a^2} = 0.1 \times 10^8$  dynes, where  $d$  is the force-constant of Cl-P-Cl angular deformation. The calculated value of P-Cl force-constant is in good agreement with the value to be expected on the basis of the dissociation energy of the compound and the P-Cl distance.

## 1 INTRODUCTION

Moureu, Magat and Wettröf (1938) have made a spectroscopic study of the structure of liquid  $\text{PCl}_3$ , and have come to the conclusion that in the liquid and vapour states the substance exists in the form of a triangular bi-pyramid. These authors have studied the Raman spectra of  $\text{PCl}_3$  in the solid, liquid and vapour states, and have also studied the polarisation characters of Raman lines. Their results are as follows

TABLE 1

Liquid	100 (10) P	190 (7d) 6/7	271 (6.3s) 6/7	392 (6.5s) P	449 (2d) 6/7	495 (2d) 6/7
Solid			224	356	409	450
Vapour	90		226		400	
Solution in $\text{PCl}_5$ -	96 P	189 6/7		351 P	396 P	

The selection rules for the triangular bi-pyramid model (Wilson 1934) give six Raman lines of which two should be polarised and four depolarised. As this

number is observed for the liquid, these authors conclude in favour of bi-pyramidal model for the molecule of liquid  $\text{PCl}_5$ . It appears quite justifiable to assume that frequencies 449 (2d) and 495 (2d) are not independent characteristic frequencies but are due to a Fermi splitting of a characteristic frequency at 461, because  $190 + 271 = 461$ . The observed number is thus even less than that required for the triangular bi-pyramid model. We find that the spectroscopic results are not in favour of the triangular bi-pyramid model, on the contrary, they suggest a square pyramid model for the liquid molecule.

It is possible to calculate the P-Cl and Cl-Cl force constants in the molecule by assuming the two totally symmetric vibrations of the triangular bi-pyramid model to be 100 and 392. The values of the P-Cl and Cl-Cl force constants will depend on the P-Cl and Cl-Cl distances. According to Magat, Mourou and Wetloff (1939), the P-Cl distance is 2.09 Å U and the Cl-Cl distances are 2.96 and 3.62 Å U. Rouault (1938) finds from the electron diffraction studies in  $\text{PCl}_5$  vapour that the minimum Cl-Cl distance is 3.08 Å U, and takes the P-Cl distances as 2.1 and 2.25 Å U. According to Brockway and Beach (1938), P-Cl distance in  $\text{PCl}_5$ ,  $\text{POCl}_3$  and other phosphorus compounds is 2.02 Å U, while the Cl-Cl distance is 3.08 Å U in  $\text{PCl}_5$  and 3.22 Å U in  $\text{POCl}_3$ . One may, therefore, reasonably expect the P-Cl force constant in  $\text{PCl}_5$  to be less than that in  $\text{PCl}_3$ , where its value, according to the calculations of Howard and Wilson (1931) is  $2.1 \times 10^5$  dynes.

## 2. CALCULATION OF FORCE CONSTANTS FOR THE TRIANGULAR BI-PYRAMID MODEL.

Assuming the triangular bi-pyramid model for the molecule, the three chlorine atoms (1), (2), (3) lie in one plane at the corner of an equilateral triangle with the phosphorus atom (6) in the centre. The two remaining chlorine atoms (4) and (5) form two pyramids on either side of the triangle so as to keep the plane of symmetry in the triangle. The system belongs to the point group  $D_{3h}$ , and the two polarised Raman lines are the two totally symmetric vibrations ( $\nu_1$  and  $\nu_2$ , those that preserve all the elements of symmetry) of this point group. These are (a) one in which the three chlorine atoms (1), (2), (3) move along the P-Cl valence bonds, all towards or away from the phosphorus atom (6), and (b) the other in which the chlorine atoms (4) and (5) move towards or away from the phosphorus atom (6).

For finding the force constants we consider two different cases (i) one in which all the P-Cl bonds in the molecule have the same length and (ii) the other in which the P-Cl distance outside the plane of chlorine atoms (1), (2), (3) is different from the P-Cl distance in the plane.

The most general potential energy function for the totally symmetric vibrations may be written as

$$k \Delta r_{16}^2 + k^1 \Delta r_{46}^2 + k_1 \Delta r_{11}^2 + k_2 \Delta r_{12}^2$$

where  $k$  and  $k^1$  are the force constants of P-Cl valence in the plane and outside the plane of chlorine atoms (1), (2), (3),  $k_1$  and  $k_2$  the Cl-Cl force constants outside and in this plane and  $\Delta r_{ij}$  is the variation of the distance  $r_{ij}$  between the atoms  $i$  and  $j$ . If the displacements in the two symmetry modes (a) and (b) given above be  $\alpha$  and  $\beta$  respectively, the potential energy  $V$  and the kinetic energy  $T$  are given by

$$2V = 3k \alpha^2 + 2k^1 \beta^2 + 3k_2 (\sqrt{3}\alpha)^2 + 6k_1 \left( \frac{\beta + \alpha}{\sqrt{2}} \right)^2$$

$$2T = 3m_1 \dot{\alpha}^2 + 2m_1 \dot{\beta}^2$$

The frequencies  $\omega_1$  and  $\omega_2$  are given by the expressions

$$\frac{k}{m_1} (1+x) + \frac{6x+5}{2} \frac{k_1}{m_1} = \lambda_1^2 + \lambda_2^2 \quad (1)$$

$$\frac{k^2}{m_1^2} x + \frac{k k_1}{m_1^2} \left( \frac{6x+3+2x}{2} \right) + \frac{9}{2} x \frac{k_1^2}{m_1^2} = \lambda_1^2 \lambda_2^2$$

where  $(k_2/k_1) = x$ ,  $(k^1/k) = x$  and  $\omega$  (in  $\text{cm}^{-1}$ ) =  $\frac{\lambda}{2\pi c}$ ,  $c$  being the velocity of light

For finding  $k_2/k_1$  we use the Cl-Cl force constants calculated by Nath (1934) for various tetra-chlorides (Table 2). If we assume the Cl-Cl distances

TABLE 2

	Cl-Cl force constant	Inter-nuclear Cl-Cl distance
C $\text{Cl}_4$	$645 \times 10^5$ dynes	$2.98 \text{ \AA}^\circ$
Si $\text{Cl}_4$ ..	$283 \times 10^5$ ..	$3.29 \text{ \AA}^\circ$
Ge $\text{Cl}_4$	$232 \times 10^5$ ..	$3.43 \text{ \AA}^\circ$
Ti $\text{Cl}_4$	$155 \times 10^5$ ..	$3.61 \text{ \AA}^\circ$
Sn $\text{Cl}_4$	$129 \times 10^5$ ..	$3.81 \text{ \AA}^\circ$

in the  $\text{PCl}_5$  molecule to be 2.96 and 3.62 (Moureu, Magat) the above table gives  $(k_2/k_1) = \frac{1}{2}$ , whereas if we take these distances as 3.08 and 3.62



(Rouault) we find  $(k_2/k_1) < \frac{1}{2}$ . We solve equation (1) for  $k$ ,  $k^1$  and  $k_1$  for different values of  $\alpha$  ( $k_2/k_1$ ) and  $\alpha$  ( $k^1/k_1$ ). For  $\alpha=1$  we obtain the solution for case (i) in which all the P-Cl bonds have the same length. Table 3 shows the results of calculation for cases (i) and (ii) separately.

TABLE 3

Case (i)				Case (ii)							
$\alpha \rightarrow$	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	0	$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{4}$	$\frac{1}{5}$	$\frac{1}{6}$	$\frac{1}{7}$	$\frac{1}{8}$
$\alpha \rightarrow$	1	1	1		0.5	1		0.5	1	0.5	1
$k \times 10^{-5}$	3.67	3.80	3.96	3.2	3.13	3.33	3.12	3.36	3.09	3.4	dynes
$k^1 \times 10^{-5}$	3.67	3.80	3.96	21	156	333	156	336	154	34	
$k_1 \times 10^{-5}$	-1.21	-1.20	-1.12	0	+0.35	-0.8	0.35	-0.83	0.4	-0.85	

For case (i) we find that the calculated values of P-Cl and Cl-Cl force constants are very much higher than the expected values, and the latter force-constants are also negative. It follows that the structure as represented by case (i) does not fit in with the experimental data.

For case (ii) the value of P-Cl force constant in the plane of Cl atoms (1), (2), (3), i.e.,  $k$  is in all cases much greater than  $2.1 \times 10^5$ . Further for a positive value of  $k_1$  (Cl-Cl force constant) the value of  $\alpha$  ( $k^1/k$ ) is less than 1, i.e.,  $k > 10 k^1$ . We can reject this structure as well on the basis of the first result alone ( $k > 2.1$ ) but the second result also leads to the same conclusion. According to the Allen and Longair (1935) the force constant  $K_r$  and the inter-nuclear

distance  $R_r$  may be connected by a relation of the form  $R_r^2 = \frac{C_{12}}{(K_r)^2}$  or  $R_r^6 K_r = \text{const}$ .

We may use this relation to find the variation of P-Cl force constant with P-Cl distance. According to Rouault the P-Cl distance in the plane of the Cl atoms (1), (2), (3) is 2.1 Å while outside this plane its length is 2.25 Å. The P-Cl force constants in the two cases are  $k$  and  $k^1$  respectively. Therefore  $(2.25)^6 k^1 = (2.1)^6 k$  or  $k/k^1 = 1.5$ . Thus for a bond length 2.25 Å the value of P-Cl force constant  $k^1$  should be  $k/1.5$ . By calculation on the basis of triangular bi-pyramid structure  $k^1 < k/10$ . We are therefore justified in assuming that the triangular bi-pyramid structure is not in accordance with the spectroscopic data.

The triangular bi-pyramid model will have zero dipole moment but Lunell (1936) finds that in  $\text{CCl}_4$  solution the substance shows a dipole moment of 87 D. This is in agreement with our deduction that the spectroscopic results do not support the triangular bi-pyramid model for the liquid molecule. Ronault has suggested the triangular bi-pyramid structure for the vapour molecule, but as the spectroscopic results for the vapour state are very incomplete, nothing can be stated definitely about it. However, it will be worth while to note an observation of Brockway and Beach on the electron diffraction study of  $\text{PF}_5$  gas 'that the square pyramid model and the triangular bi-pyramid model both show good agreement with photographs and the choice between the two models cannot be made on electron diffraction results.

### 3 SQUARE PYRAMID MODEL

We shall now examine the square pyramid model as an alternative structure. Let the chlorine atoms at the four corners of a square be called (1), (2), (3), (4) in succession, the chlorine atom outside the square on a normal to the plane passing through the centre as (5) and the phosphorus atom at the centre of the square as (6). The system belongs to the point group  $C_{4v}$ . The character table, number of modes of vibration and their selection rules in the Raman Effect and infra-red are given below in Table 4.

TABLE 4

$C_{4v}$	E	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$n$	T	$n'$	Selection rules	
									Raman	Infra-red
A	1		1	1	1	1	Q	3	pol	a
B	1	1	1	-1	-1	1	$Q_{xz}$	0		
C	1	1	1	1	-1	2	0	2	dep	f
D	1	-1	1	-1	1	1	0	1	dep	f
E	2	0	-2	0	0	5	$Q_{xx}, Q_{yy},$ $Q_{xy}, Q_{yz},$	3	dep	a
$n_R$	6	2	2	4	2	for the whole molecule				
$n_{IR}$	18	4	-2	8	4					

a—active, f—forbidden, dep—depolarised

The table shows that we should expect nine lines of which three should be polarised and six depolarised. The fact that this number is not observed is most likely due to experimental difficulties because, as the calculation shows, several frequencies lie within  $150\text{ cm}^{-1}$ .

We shall now calculate the force constants by assuming three polarised frequencies 100 350 396 as belonging to class A and then evaluate the remaining frequencies. For this purpose we have to write the symmetry co-ordinates in terms of the co ordinates of atoms referred to their equilibrium positions as origin. If  $x, y, z$  be the co ordinates of the  $i$ th atom with respect to its position of rest as origin then for the atoms (1) (2) (3) (4) positive  $x$  points towards the phosphorus atom (5) at the centre positive  $z$  points upwards perpendicular to the plane of the square and  $y$  is at right angles to both such that the motion is right handed. For atoms (5) and (6)  $Z_5$  and  $Z_6$  represent motions perpendicular to the plane of the square while  $X_5, X_6$  and  $Y_5, Y_6$  represent motions parallel to the  $x$  and  $y$  axes respectively. The symmetry co ordinates are

$$\begin{array}{ll}
 Q \rightarrow m_1^{\frac{1}{2}} (x_1 + x_2 + x_3 + x_4 + Z_5) + \frac{1}{\sqrt{5}} Z_6 & \\
 Q'_{12} \rightarrow x_1 + x_2 + x_3 + x_4 & \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{A } 4 \\
 Q'_{13} \rightarrow m_1^{\frac{1}{2}} (x_1 + x_2 + x_3 + x_4 + Z_5) - \frac{1}{\sqrt{5}} Z_6 & \\
 Q'_{14} \rightarrow x_1 + x_2 + x_3 + x_4 - 4Z_5 & \\
 Q_{15} \rightarrow y_1 + y_2 + y_3 + y_4 & \text{B } 1 \\
 Q'_{16} \rightarrow x_1 + x_2 - x_3 - x_4 & \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{C } 2 \\
 Q'_{17} \rightarrow x_1 + x_2 - x_3 - x_4 & \\
 Q'_{18} \rightarrow y_1 + y_2 - y_3 - y_4 & \text{D } 1 \\
 Q_x \rightarrow m_1^{\frac{1}{2}} (y_1 - x_2 - y_3 + x_4) + m_1^{\frac{1}{2}} X_5 + m_2^{\frac{1}{2}} X_6 & \\
 Q_y \rightarrow m_1^{\frac{1}{2}} (x_1 + y_2 - x_3 - y_4) - m_1^{\frac{1}{2}} Y_5 - m_2^{\frac{1}{2}} Y_6 & \\
 Q_u \rightarrow m_1^{\frac{1}{2}} c (x_1 + y_2 - x_3 - y_4) + m_1^{\frac{1}{2}} (a-c) Y_5 - m_2^{\frac{1}{2}} c X_5 & \\
 & + m_1^{\frac{1}{2}} a (x_3 - x_4) \\
 Q_{wy} \rightarrow m_1^{\frac{1}{2}} c (y_1 - x_2 - y_3 + x_4) - m_1^{\frac{1}{2}} (a-c) X_5 + m_2^{\frac{1}{2}} c X_6 & \\
 & + m_1^{\frac{1}{2}} a (x_1 - x_4) \\
 Q'_{11a} \rightarrow (y_1 - y_2) + (x_3 - x_4) & \\
 Q'_{11b} \rightarrow (x_1 - x_2) - (y_3 - y_4) & \left. \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right\} \text{E } 5 \\
 Q'_{12a} \rightarrow m_2^{\frac{1}{2}} (y_1 - x_2 - y_3 + x_4) - 4m_1^{\frac{1}{2}} X_5 & \\
 Q'_{12b} \rightarrow m_2^{\frac{1}{2}} (x_1 + y_2 - x_3 - y_4) + 4m_1^{\frac{1}{2}} X_6 & \\
 Q'_{13} \rightarrow \frac{a-c}{2} m_1^{\frac{1}{2}} (x_2 - x_4) - cm_1^{\frac{1}{2}} y_1 - x_2 - y_3 + x_4 & \\
 & + (a-c) m_1^{\frac{1}{2}} X_5 - m_2^{\frac{1}{2}} c X_6 \\
 Q'_{14b} \rightarrow \frac{a-c}{2} m_1^{\frac{1}{2}} (x_1 - x_3) - cm_1^{\frac{1}{2}} (x_2 + y_3 - x_4 - y_4) & \\
 & - (a-c) m_1^{\frac{1}{2}} Y_5 + m_2^{\frac{1}{2}} c Y_6
 \end{array}$$

where 'a' is the P-Cl distance, 'c' the distance of the centre of gravity of the square pyramid model above the central atom (6) [ $c = am_1/(5m_1 + m_2)$ , where  $m_1$  is the mass of the chlorine atom and  $m_2$  that of the phosphorus atom]

For the formulation of the potential energy function we use only three force constants, viz  $k$  that of the primary valence P-Cl,  $k_1$  of the repulsion between the Cl-Cl atoms, and  $d$  the force constant of angular Cl-P-Cl deformation. The calculation of force constants and frequencies is given below.

*Class A* If  $\alpha, \beta$  and  $\gamma$  are the displacements in the three modes  $Q'_2, Q'_3$  and  $Q'_4$ , the potential energy is given by

$$\phi V = 4k\alpha^2 + k(p\beta - 4\gamma)^2 + 4k_1(\sqrt{2}\alpha)^2 + 4k_1\left(\frac{\alpha + 5\gamma}{\sqrt{2}}\right)^2 + \frac{4d}{a^2}(p\beta + \gamma)^2$$

where

$$p = (m_2 + 5m_1)/m_1^{\frac{1}{2}} m_2^{\frac{1}{2}}$$

and the kinetic energy by  $4m_1\alpha^2 + (5m_1 + 25m_2)\beta^2 + 20m_1\gamma^2$

The frequencies are given by the determinant

$$\begin{vmatrix} 4k + 10k_1 - 4m_1\lambda^2 & 0 & 10k_1 \\ 0 & 39.5k + 158d' - 5(m_2 + 5m_1)\lambda^2 & -25.15(k - d') \\ 10k_1 & -25.15(k - d') & 16k + 50k_1 + 4d' - 20m_1\lambda^2 \end{vmatrix} = 0$$

where

$$d' = d/a^2$$

*Class C* The two frequencies  $Q'_6, Q'_7$  are given by the determinant

$$\begin{vmatrix} 4k + 2k_1 - 4m_1\lambda^2 & 2k_1 \\ 2k_1 & 2k_1 + 4d' - 4m_1\lambda^2 \end{vmatrix} = 0$$

*Class D* The single frequency  $Q_8$  is given by  $\lambda^2 = (2k_1 + 4d')/m_1$ .

*Class E* The frequencies  $Q'_{11a}, Q'_{12a}, Q'_{13a}$  are given by the determinant

$$\begin{vmatrix} 2k + 9k_1 + 4d' - 4m_1\lambda^2 & -(10.43k + 9346k_1 - 20.86d') & l_1 \\ -(10.43k + 9346k_1 - 20.86d') & 54.4k + 8735k_1 + 145.4d' & -(9346k_1 - 8.56d') \\ & -(16m_1 + 4m_2)\lambda^2 & \\ l_1 & -(9346k_1 - 8.56d') & l_1 + 2d' - \frac{2m_1\left(1 - \frac{c}{a}\right)\lambda^2}{3 - \frac{c}{a}} \end{vmatrix} = 0$$

If we take  $k = 1.53 \times 10^5$ ,  $k_1 = 0.2 \times 10^5$ ,  $d' = 0.01 \times 10^5$  dynes, we get the frequencies given in the second column of Table 5. Observed frequencies are also given for comparison.

Class	Frequencies calculated	Frequencies observed
A	410, 314, 123	396, 351, 96 in solution 392, ( ), 100 in liq $\text{PCl}_5$
C	280, 70	271, ( )
D	146	(190)
E	447, 155, 116	449, 495, ( ), ( )

The agreement between the observed and calculated values is fairly good and the values of the force constants obtained are quite reasonable. The value of P-Cl force constant is less than that in  $\text{PCl}_3$ , as the P-Cl distance in  $\text{PCl}_5$  is greater than that in  $\text{PCl}_3$ . The Cl-Cl force constant is positive and of the right order. The calculation also shows that the missing frequencies are near the exciting line, and so there is a likelihood of their being masked on account of the back-ground. The experimental observations, therefore fit in with the square pyramid model. From chemical evidence (*ie*, reactions of  $\text{PCl}_5$  with indene, styrol, asymmetric diphenyl ethylene) Bergmann and Bondi (1951) conclude in favour of the square pyramid model for the molecule of liquid  $\text{PCl}_5$ . Redlick, Kürz, and Rosenfeld have proposed the same structure for the molecule of liquid  $\text{SbCl}_5$ .

Sutherland (1938) has shown that the dissociation energy, of a linkage, is given, by  $D = \frac{K_r R_r^2}{mn}$  where D is the dissociation energy,  $R_r$  the inter-nuclear distance between the atoms and  $K_r$  the force constant between them and  $m$  and  $n$  are constants. Mecke (1931) also proposed the same relation. Using this relation it is possible to compare the values of P-Cl force constants in  $\text{PCl}_3$  and  $\text{PCl}_5$ . Thus

$$\frac{D_{\text{PCl}_5}}{D_{\text{PCl}_3}} = \frac{K_{\text{P-Cl}(5)} R_{\text{P-Cl}(5)}^2}{K_{\text{P-Cl}(3)} R_{\text{P-Cl}(3)}^2}, \text{ where } R_i \text{ is the P-Cl distance}$$

The value of the P-Cl distance in  $\text{PCl}_3$  is 2.02 Å (Brockway and Beach) and in  $\text{PCl}_5$  its value may be taken as 2.1 Å (Ronault). The P-Cl force constant in  $\text{PCl}_3$  is  $2.1 \times 10^5$  dynes (Howard and Wilson). According to Jan Khan and Samuel (1936) the dissociation energy of the P-Cl linkage in  $\text{PCl}_3$  is 8 K Cal while in  $\text{PCl}_5$  its value is only 69 K Cal. Substituting these values in the above equation the value of  $K_{\text{PCl}_5}$  comes out as  $1.54 \times 10^5$  dynes. This compares very well with the value of  $K_{\text{PCl}_5} = 1.53 \times 10^5$  calculated with the help of spectroscopic data on the basis of the square pyramid model.

We may also use Allen-Longair's relation to compare the P-Cl bond strength in  $\text{PCl}_3$  and  $\text{PCl}_5$ . We have

$$K_{\text{PCl}_5} \times R_{\text{PCl}_5}^6 = K_{\text{PCl}_3} \times R_{\text{PCl}_3}^6$$

Substituting in this equation the values of  $K$  and  $R$  as given in the previous paragraph we have  $\frac{2.1}{1.53} = (2.1/2.02)^6$ . The left-hand side is equal to 1.37 while the right-hand side is equal to 1.26. These considerations show that the value of  $K_{\text{PCl}_5} = 1.53 \times 10^5$  is very nearly the correct value, and agrees with that to be expected on the basis of the value of the inter-nuclear distance and the dissociation energy of the molecule. They thus lend additional support to the square pyramid structure for the molecule of the liquid  $\text{PCl}_5$ .

#### 4 SUMMARY

The Raman frequencies for liquid  $\text{PCl}_5$  spectrum are examined and assuming the structure to be triangular bi-pyramid, the force constants of P-Cl valence, Cl-Cl repulsion are calculated by using the two polarised Raman frequencies 392 and 100  $\text{cm}^{-1}$ . It is found that the value of P-Cl force constant, if we assume that all the P-Cl bonds in the molecule have the same length, is  $3.67 \times 10^5$  dynes which is higher than the corresponding value  $2.1 \times 10^5$  dynes in  $\text{PCl}_3$  although the P-Cl distance in  $\text{PCl}_5$  is greater than that in  $\text{PCl}_3$ . Further, the Cl-Cl force constant is negative while it is positive in other compounds. The case, in which the P-Cl distance outside the plane of Cl atoms (1), (2), (3) is greater than the P-Cl distance in the plane, has also been considered and leads to similar results. It was found by the use of Allen-Longair's relation that in this case the ratio of the calculated values of P-Cl force constants is very different from what one would expect on the basis of the P-Cl distances. These considerations and those of dipole moments enable us to discard the triangular bi-pyramid model.

The square pyramid model in which the phosphorus atom is at the centre of a square with four chlorine atoms at the corners and the fifth chlorine atom is outside the square is next considered. Using  $k$  (P-Cl) force constant  $1.53 \times 10^5$  dynes, Cl-Cl force constant  $= 2 \times 10^5$  dynes and  $d' = \frac{d}{a}$ , the Cl-P-Cl deformation force  $= 0.1 \times 10^5$  dynes, the frequencies calculated for class A are 410, 314, 123 (obs. 396, 351, 96, 392, ( ), 100), for class C, 280, 70, (obs. 271, ( )), for class D, 146 (obs. 190); and for class E, 497, 155, 116 (obs. 405, 449, ( ), ( ))

A fairly close agreement between the observed and the calculated frequencies and the reasonable values of force constants obtained justify the proposed structure. Further the calculated value of P-Cl force constant is in good agreement with that to be expected on the basis of the dissociation energy of the compound and the P-Cl distance.

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# THE CRYSTAL STRUCTURES AND THE SPACE GROUPS OF SOME AROMATIC CRYSTALS

## I—PHLOROGLUCINOL DIHYDRATE, $s\text{-C}_6\text{H}_3(\text{OH})_3 \cdot 2\text{H}_2\text{O}$

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### [PLATE 1]

Phloroglucinol dihydrate crystallizes in the orthorhombic system. Its unit cell has the dimensions

$$a = 8.75 \quad b = 8.10, \quad c = 13.51 \text{ \AA}$$

and it contains 4 molecules of  $\text{C}_6\text{H}_3(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ . The crystal habit is pseudo hexagonal, with 'a' as the pseudo hexagonal axis.

The observed characteristic extinctions in X-ray reflections are

$$(0kl) \text{ with } (k+l) \text{ odd}$$

$$(h0l) \text{ with } h \text{ odd,}$$

which point to the space group being either  $Q_6^{12}$  or  $C_{2v}^{12}$ . Since these space groups belong to the bipyramidal and the pyramidal classes respectively, observations on the external form of the crystal should enable us to decide between the two space groups. But unfortunately the pyramidal faces do not appear on the crystals. From other considerations, however, the space group  $Q_6^{12}$  can be definitely ruled out. This space group requires the molecule to possess either a centre of symmetry, or a plane of symmetry parallel to (001), a centre of symmetry for the molecule will be inconsistent with its chemical formula, and a plane of symmetry parallel to (001) inconsistent with the observed X-ray reflections, and also with the magnetic and optical properties of the crystal. The only other space group that can fit with the observed extinctions namely  $C_{2v}^{12}$ , should therefore be regarded as the correct space group for the crystal.

### 1 INTRODUCTION

Extensive measurements\* have been made during recent years by Professor Krishnan and his collaborators, Mrs Lonsdale, and others, on the magnetic and other properties of single crystals of aromatic compounds, and the results obtained have been discussed by them in relation to the orientations of the benzene rings in these crystals. For some of the crystals a detailed knowledge of the crystal structure† is available from the X-ray studies made by Robertson, Mrs Lonsdale, Miss Knaggs, and others, for some others the dimensions of the unit cell and the space group are known; while for the majority of them the available crystallographic data are meagre. We have, therefore, undertaken a

\*See K. Lonsdale, *Reports on Progress in Physics*, 4 (1938), 368

†See J. M. Robertson, *ibid.* 4 (1938), 332



systematic study of the space groups of these crystals, and the results will be published in a series of papers of which this is the first. The present paper concerns itself with the determination of the space group of phloroglucinol dihydrate.

Phloroglucinol dihydrate crystallizes in the orthorhombic system. Well-developed single crystals are easily grown by the slow evaporation of a solution of the substance in ether or absolute alcohol. They appear as thick, transparent six-sided tabular plates parallel to {001} and bounded by {201} and {110}. Occasionally {100} is also developed and imperfect cleavage has been observed along this plane. This compound is soluble in water and crystals grown out of aqueous solutions, while retaining the same axial ratios, show a remarkably different habit, in which {011}, {001} and {201} are found to be developed. The latter crystals present a pseudo-hexagonal appearance, with the pseudo-hexagonal axis along 'a'.

The present X-ray studies on phloroglucinol dihydrate were undertaken with the view of verifying whether these two types of crystals were crystallographically identical. Rotation photographs about the three crystallographic axes showed definitely that this was the case. This conclusion is supported by the optical measurements made by the present writer and by the magnetic measurements made by Santilal Banerjee (1938), which gave identical results for the two types of crystals. In the course of these X-ray studies it was found that the earlier analysis of the structure of this crystal and the space group assigned to it, namely  $Q_1^{12}$ , in the orthorhombic bipyramidal class (K. Banerjee and R. Ahmad, 1938), do not agree with observation. The present paper gives an account of fresh X-ray studies made on the crystal, and a critical discussion of its space group in relation to these and other available data.

## 2. THE UNIT CELL

Goniometric measurements (see Table I) made with a large number of well-developed crystals, grown from different solvents, gave

$$a \cdot b \cdot c = 0.8333 \quad 1 \cdot 1.066$$

X-ray rotation photographs taken about the 'a', 'b' and 'c' axes using the  $K_{\alpha 1}$  radiation of copper (see Figs. a, b, c in Plate 1), gave the following dimensions for the unit cell of the crystal.

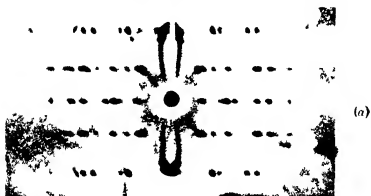
$$a=6.75, \quad b=8.10, \quad c=13.51 \text{ \AA.}$$

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\*The crystals are slightly coloured and pleochroic, the colour being more conspicuous in crystals grown from aqueous solutions. The colour is presumably due to traces of the oxidation products.

PLATE I

S. I. CHIRCHAK—*The Crystal Structure and the Space Group of Phloroglucinol Dihydrate*



(a)



(b)



(c)

Rotational photographs of Phloroglucinol Dihydrate

(a) about *a* AXIS  
(b) about *b* AXIS  
(c) about *c* AXIS



TABLE I

		Observed	Calculated	Calculated from axial ratios of	
				Banerjee & Ahmad	Groth
(110)	(110)	79° 6'	—	79° 57'	79° 1'
(001)	(011)	59° 6'	59° 5'	59° 24'	59° 10'
(001)	(101)	75° 38'	—	76°	76° 6'
(201)	(101)	54°	54°	77° 0'	77° 8'
(011)	(011)	61° 45'	61° 50'	61° 1'	60° 40'
(201)	(011)	82° 53'	82° 50'	82° 5'	81° 12'
(201)	(110)	—	—	—	41° 5'

The density of the crystal determined by the floatation method was  $\rho = 1.456$  gm/cc which gives for the number of molecules of  $C_{10}H_{10}(OH)_2 \cdot H_2O$  in the unit cell 4.0. The above axial dimensions lead to

$$a : b : c = 0.933 : 1 : 1.667$$

which agree well with the goniometric ratios given above but differ appreciably from those given by Groth (1917) namely

$$a : b : c = 0.8246 : 1 : 1.7086$$

K. Banerjee and R. Ahmad (1938) who have made X-ray measurements on this crystal give for the dimensions of the unit cell

$$a = 6.79 \text{ \AA} \quad b = 8.10 \text{ \AA} \quad c = 13.70 \text{ \AA}$$

and for the density the value  $1.391$  gm/cc\*

### 3. DETERMINATION OF THE SPACE GROUP

Rotation photographs and oscillation photographs over suitably small ranges of oscillation about the three crystallographic axes show that the reflections from the following planes are absent (see Table II) —

$$(0kl) \text{ if } (l + k) \text{ is odd,}$$

$$(h0l) \text{ if } h \text{ is odd}$$

The reflections from all other planes were in general normal showing that the underlying lattice is simple orthorhombic.

\*Since the paper was written there has appeared in the *Indian Journal of Physics* for June, 1942, Vol. 17 p. 163 a paper by C. R. Bose and Ranjit Kumar Sen on the axial dimensions of this crystal and it is gratifying that the axial dimensions and the density given by them agree well with ours. Their values are

$$a = 6.740 \text{ \AA} \quad b = 8.090 \text{ \AA} \quad c = 13.60 \text{ \AA}, \quad \rho = 1.453 \text{ gm/cc}$$

TABLE II

<i>hkl</i>	Intensity	<i>hkl</i>	Intensity	<i>hkl</i>	Intensity
200	a	051	wm—	802	vw
400	a	053	vw	110	m
600	a ?	055	vw	120	wm
800	w	057	vw	130	m—
020	m	059	vw	140	a
040	wm+	05(11)	vw	150	vw
060	a ?			160	w+
080	w—	062	vw	170	vw
002	m	064	vw+	210	w—
004	w	068	vw	220	vw—
006	ms	06(10)	vw	230	wm+
008	wm+			240	a
00(10)	wm+	071	vw	250	w+
00(12)	wm	073	vw	270	w
00(14)	vw	075	vw	280	i
		079	vw		
011	wm			310	a
013	ms	082	vw	320	wm
015	m—	084	vw	330	wm
017	vw	086	vw	340	vw
019	wm			350	vw
		201	vs	360	w—
022	m+	203	w	370	vw
024	m—	205	m		
026	wm	207	a ?	420	w
028	m—	209	m	440	w
02(10)	vw	211	a	460	vw
		213	vw	480	vw
031	wm+	215	w		
033	ms	217	w	510	w
035	wm+	219	w	530	vw
037	w	402	w+	550	vw
039	w	404	vw	560	vw
03(11)	vw	406	w		
		408	vw	610	vw—
042	w	40(10)	w	630	vw
044	vw	40(12)	wm	650	vw
046	w				
048	a	601	w		
04(10)	vw	603	vw—	730	vw
04(12)	w+	605	vw		

TABLE III

<i>hkl</i>	Intensity	<i>hkl</i>	Intensity	<i>hkl</i>	Intensity
111	wm +	158	vw	241	wm
112	wm	159	vw -	243	vw
113	w	15(10)	vw -	245	vw
114	wm +			247	vw
115	m			249	vw
116	wm	161	vw	25(11)	vw
117	w	162	vw		
118	vw	163	vw	251	a
119	vw	164	vw	252	vw -
11(10)	vw	165	wm	254	vw
11(11)	vw	166	wm	256	vw
		167	w	258	vw
121	wm			25(10)	vw
122	w -	211	vw	25(11)	vw
123	vw	212	ms		
124	wm -	213	a	272	vw
125	m -	214	vw +	274	vw -
126	wm	215	a	276	vw
127	w	216	w		
		217	a	281	vw
131	m -	218	w	285	vw
132	w	219	a		
133	m -	21(10)	vw	311	w +
134	vw	21(11)	a	312	w -
135	wm			313	vw
136	w	221	wm	314	vw
137	vw	222	a ?	315	w
138	vw	223	m	316	vw
139	vw	224	a	317	vw
13(10)	vw	225	vw -	319	vw
		226	a	31(10)	vw
141	vw	227	vw	31(11)	vw
142	w +	229	vw		
143	w	22(10)	a	321	vw
144	vw	22(11)	vw	322	a ?
145	vw			323	vw
146	vw	231	a	324	vw
148	vw	232	w +	325	vw
149	vw	233	a	326	w
14(10)	vw	234	vw	327	vw
14(11)	vw	235	a	329	vw
		236	w	32(10)	vw
151	a	237	a		
152	vw +	238	vw	331	vw
153	w +	239	a	332	vw
154	vw	23(10)	vw	333	vw
155	a	23(12)	vw	334	w
157	w			335	vw

<i>hkl</i>	Intensity	<i>hkl</i>	Intensity	<i>hkl</i>	Intensity
336	vw	422	vw	524	vw
337	vw	424	vw	525	vw
338	vw	428	vw		
33(10)	vw	431	vw	531	vw
341	a	433	w-	538	vw
342	vw	435	vw-	535	vw
343	w-	439	vw	541	vw
345	vw	43(11)	vw	542	vw
				543	vw
352	vw	442	vw		
353	w	444	vw	561	vw
354	vw			562	vw
		451	vw	563	vw
361	vw-	455	w	564	vw-
363	vw			565	w
364	vw+	462	vw		
365	w	464	vw	612	vw
378	vw	473	vw	621	vw
374	vw-	475	w	623	vw
384	vw-	511	vw	632	vw
		512	vw-	634	vw
411	vw	513	vw	636	vw
413	w	514	vw		
415	vw	515	vw	641	vw
417	vw	516	vw	645	vw-
419	vw				

The absences noted above are characteristic of the space groups

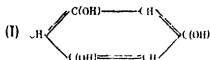
$Q_4^{16}$  ( $Pnam$ ) in the holohedral class, and

$C_{2v}^9$  ( $Pna$ ) in the hemihedral class.

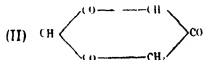
Observations on the external form of the crystal should enable us to decide between these two classes and hence between the two space groups. But unfortunately, though we have grown crystals out of several solvents, in none of them could we observe any pyramidal faces that would help us to settle the crystal class. If the crystal should prove to be pyramidal only, *i.e.* if there were no real plane of symmetry parallel to (001), the space group would be  $C_{2v}^9$  ( $Pna$ ), with a glide-plane of translation  $(b+c)/2$  parallel to (100), a glide-plane of translation  $a/2$  parallel to (010), and a two-fold screw-axis parallel to 'c'. On the other hand, if the crystal were bipyramidal, the space group would be  $Q_4^{16}$  ( $Pnam$ ), in which case in addition to the glide-planes given above, each of the four molecules in the unit cell must possess either a centre of symmetry, or a plane of symmetry parallel to (001).

#### 4 EVIDENCE FOR THE HEXAGONAL RING IN THE MOLECULE OF PHLOROGLUCINOL DIHYDRATE BEING BENZENIC

There has been a long-standing controversy among the organic chemists regarding the molecular structure of phloroglucinol. In most of its reactions it behaves like a trihydric phenol.



On the other hand, it unites with three molecules of hydroxylamine to form a trioxime, so that it may also be considered a triketone 1,3,5-triketohexamethylene, having the structural formula



The benzenic structure I should exhibit an abnormal diamagnetism directed along the normal to the plane of the benzene ring, and hence also a large magnetic anisotropy. It will have similarly a large optical anisotropy as well. On the other hand, structure II may not be planar at all, and will be nearly isotropic both magnetically and optically, in striking contrast with I.

Santalal Banerjee (1938) has made magnetic susceptibility measurements on single crystals of phloroglucinol dihydrate. He finds that the principal susceptibilities of the crystal per gram molecule have the values

$$\chi_a = -120.1 \times 10^{-6}, \quad \chi_b = -83.1 \times 10^{-6}, \quad \chi_c = -81.1 \times 10^{-6},$$

giving for the mean gram molecular susceptibility of the crystal the value  $\chi_m = -95.8 \times 10^{-6}$ . The large magnetic anisotropy of the crystal, and the above value of the mean susceptibility, as pointed by Santalal Banerjee, are definitely in favour of the benzenic structure I for the molecule.

Measurements of the principal refractive indices of the crystal made by the present writer give for the D lines of sodium

$$\alpha = 1.416, \quad \beta = 1.670, \quad \gamma = 1.718, \quad V = 71^\circ 40'$$

$$a = \alpha, \quad b = \gamma, \quad c = \beta$$

These data also strongly support the benzenic structure for the molecule.

Incidentally it may be noted that both the magnetic and the optical data are in conformity with the 'a' axis of the crystal being a pseudo-hexagonal axis.



5. REASONS FOR RULING OUT THE SPACE GROUP  $Q_4^{16}$ 

We have seen that the crystal of phloroglucinol dihydrate belongs either to the space group  $Q_4^{16}$  or to the space group  $C_{2v}^8$ . We now proceed to give the reasons for excluding the former space group, namely  $Q_4^{16}$ .

If the space group were  $Q_4^{16}$ , each of the four molecules in the unit cell of the crystal must possess either a centre of symmetry, or a plane of symmetry parallel to (001). Now the chemical formula for the molecule, with three (OH) groups in symmetrical positions, definitely excludes a centre of symmetry. The plane of symmetry for the molecule is also ruled out for the following reasons:

If the molecule of phloroglucinol dihydrate were to possess a plane of symmetry, then consistent with the known structure of the benzene ring this plane should be either of the following —

(1) It may be parallel to the ring. Such a plane of symmetry has been observed, for example, in the molecule of *m*-dinitrobenzene (Hertel and Schneider, 1930, Hendricks, 1931, K. Banerjee and M. Ganguly, 1940). Since the X-ray data require that this symmetry plane should also be the (001) plane of the crystal, we are then forced to place all the benzene rings in the crystal of phloroglucinol dihydrate parallel to (001). This placement, however, is definitely inconsistent with observation: (i) the reflection from (002) is by no means intense, nor does the intensity of higher order reflections from this plane fall off normally, (ii) the above placement requires the 'c' axis to be both magnetically and optically an axis of symmetry such that  $|\chi_c| = |\chi_l| \approx |\chi_a|$ ,  $\alpha \approx \infty$ ,  $\infty > \beta \approx \gamma$ , which are not actually the case.

(2) The plane of symmetry may be perpendicular to the plane of the benzene ring. It should be mentioned here that in none of the numerous aromatic compounds containing discrete benzene rings studied till now for their structure has such a symmetry plane perpendicular to the plane of the benzene ring been observed (see, for example, Lonsdale, 1934). This makes the postulate of a plane of symmetry perpendicular to the benzene ring in phloroglucinol dihydrate highly improbable. Apart from its improbability, the postulate of such a plane will place all the benzene rings in phloroglucinol dihydrate parallel to 'c' axis. They may all be parallel to one another and lie in the (010) plane, or in the (100) plane, or the benzene rings may take intermediate orientations, with all the benzene planes parallel to 'c'. If the molecular planes are all parallel to (010) a little calculation from the positions of the various atoms of the four molecules in the unit cell shows that the reflections from all the planes for which  $(h+k)$  is odd or  $(h+2k)$  is odd, depending upon whether the atoms lie in the axial plane or in the glide-plane parallel to it, will

all vanish whereas actually many of these reflections are observed and are quite strong. Further the orientations of the benzene rings parallel to (010) will be quite inconsistent with the  $a$  axis being a pseudo-hexagonal axis for the crystal and also incompatible with the optical and magnetic data for the crystal, because then we should have  $|\chi_b| \gg |\chi_a| \approx |\chi_c|$  and  $b = \infty \gg c \approx a$  which are not consistent with observation.

If the molecular planes are all parallel to (100) then again the reflections from planes for which  $(h+k+l)$  is odd or  $(h+l)$  is odd depending upon whether the atoms are in the (100) plane or in the glide-plane parallel to it will all vanish whereas most of these reflections are observed.

Intermediate orientations with all the benzene planes parallel to  $c$  will also be inconsistent with the X-ray data. Because then one or the other of the various  $(hk0)$  reflections observed should be very intense whereas this is not the case as will be seen from Table II in which all the reflections in this zone appear with low intensities. Moreover the intermediate orientations considered above will also be inconsistent with the  $a$  axis being an axis of pseudo hexagonal symmetry, and also with the observed optical and magnetic properties of the crystal.

We are thus forced to conclude that the molecule of phloroglucinol cannot have either a centre of symmetry or a plane of symmetry parallel to (001) and hence the crystal cannot belong to the space group  $Q_1^{16}$ .

## 6 $C_{2v}^9$ AS THE MOST PROBABLE SPACE GROUP

The only alternative left over, namely the space group  $C_{2v}^9$  should therefore be regarded as the correct space group for the crystal. In this space group the benzene rings in the unit cell may be inclined to one another, and to the axial planes also, and this space group does not require the molecule to possess any elements of symmetry.

## 7 THE LOCATION OF THE MOLECULAR PLANES

Though we have not made quantitative intensity measurements to enable us to locate the exact orientations of the benzene rings, their approximate orientations can be deduced from the visual estimates of the intensities. On an examination of the intensities given in Tables II and III it will be seen that the (201) planes have the strongest reflections, and the intensities fall off quite normally as we go to the higher orders. The reflections from the (212) planes, each one of which is close to the corresponding (201) plane, are also quite strong, and the fall of intensity again normal in the higher orders of reflection. One

may therefore presume that the orientations of the benzene planes in the crystal of phloroglucinol dihydrate will be close to (201) and (212), and very probably intermediate between them. Now the normals to these planes make the following angles with the 'a', 'b' and 'c' axes of the crystal.

TABLE IV

	<i>a</i>	<i>b</i>	<i>c</i>
(201)	14°	90°	76°
(212)	33°	70°	65°

It is gratifying that the orientations deduced by Santalal Banerjee (1938) from the magnetic data for the crystal, namely, the normals to the benzene planes making angles of 28°, 70°, and 70° respectively with the 'a', 'b' and 'c' axes, fit well with the orientations suggested above from the X-ray data. The optical properties also are roughly in quantitative agreement with the orientations suggested.

We should mention here that according to the space group  $C_{2v}^8$  assigned to the crystal of phloroglucinol dihydrate, with (100) and (010) as the glide-planes of symmetry, the 'c' axis should be a polar axis, and the crystal should therefore exhibit piezo- and pyro-electric effects. We are verifying this result.

I am greatly indebted to Professor K. S. Krishnan, F.R.S., for his continued interest and helpful advice during the progress of this work, to the King Edward Memorial Society of Nagpur for the grant of a Research Scholarship, and to the University of Allahabad for providing research facilities, and for meeting the expenses of publication of this paper.

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# PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES INDIA

(SECTION A)

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## ON THE DIFFERENTIABILITY OF STEP FUNCTIONS

By P D SHUKLA

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(Communicated by Professor A N Singh—Received November 11, 1943)

1 The object of this paper is to answer the following question proposed by Prof A. N. Singh\* —

Does the existence of  $\phi'(0)$  for a step function  $\phi(x)$  depend upon the existence of the metric density at  $x=0$  of the set of values of  $x$  corresponding to the lines of invariability of  $\phi(x)$ ?

It has been shown that the answer to this question is in the negative

2 We shall first show that the existence of the metric density is not *necessary* for the existence of the differential coefficient. Consider, for example, the step function defined below —

In the interval  $(-1, 1)$  define a set of points  $x_r$  such that  $x_r = \frac{1}{2^r}$ ,  $r=1, 2, 3,$

. Let  $\xi_{r+1}$  denote the middle point of the interval  $(x_{r+1}, x_r)$ , and let a function  $\phi(x)$  be defined as follows in the same interval  $(x_{r+1}, x_r)$

$$\phi(x) = \frac{1}{r \cdot 2^r}, \quad x = x_r = \frac{1}{2^r},$$

$$\phi(x) = \frac{1}{(r+1) \cdot 2^{r+1}}, \quad x_{r+1} \leq x \leq \xi_{r+1},$$

and

$$\phi(x) = \psi(x), \quad \xi_{r+1} \leq x \leq x_r,$$

where  $\psi(x)$  is any monotone increasing and continuous function of  $x$  with  $\psi(\xi_{r+1}) = \frac{1}{(r+1) \cdot 2^{r+1}}$  and  $\psi(x_r) = \frac{1}{r \cdot 2^r}$

\*I am indebted to Prof A N Singh for his raising the question and helping me through

Let the function  $\phi(x)$  be defined as above for all positive integral values of  $r$ . Also let  $\phi(-x) = -\phi(x)$  and  $\phi(0) = 0$ .

Then  $\phi(x)$  is an odd, monotone non-decreasing and continuous step function with  $\phi(0) = 0$ . Also the interval  $(x_{r+1}, \xi_{r+1})$  is a line of invariability of  $\phi(x)$  for  $r = 1, 2, 3, \dots$

Now, the differential coefficient  $\phi'_+(0)$  exists. For,

$$\begin{aligned}\phi'_+(0) &= \lim_{x \rightarrow 0^+} \frac{\phi(x) - \phi(0)}{x} \\ &= \lim_{x \rightarrow 0^+} \frac{\phi(x)}{x},\end{aligned}$$

and the last limit exists. Because consider any  $x > 0$ , it must then fall in the intervals  $(x_{r+1}, x_r)$  for some value of  $r$ , say for  $r = m$ ,

i.e.,

$$x_{m+1} \leq x \leq x_m$$

Then for this  $x$ , due to the monotone character of  $\phi(x)$  we have

$$0 \leq \frac{\phi(x)}{x} \leq \frac{\phi(x_m)}{x_{m+1}}$$

But

$$\frac{\phi(x_m)}{x_{m+1}} = \frac{1/m^2}{1/2^{m+1}},$$

which tends to zero with  $1/m$

Therefore,

$$\lim_{x \rightarrow 0^+} \frac{\phi(x)}{x} = 0$$

i.e.,

$$\phi'_+(0) = 0$$

Also  $\phi(x)$  is an odd function of  $x$ . Hence  $\phi'_-(0)$  also exists and equals  $\phi'_+(0)$ . Thus  $\phi'(0)$  exists and equals zero.

It shall now be shown that the metric density of the set  $x$  corresponding to the lines of invariability of  $\phi(x)$  does not exist at  $x = 0$ .

If we take

$$x = \xi_{r+1},$$

the required metric density

$$\begin{aligned}&= \lim_{r \rightarrow \infty} \frac{\sum_{n=1}^{\infty} (\xi_{r+n} - x_{r+n})}{\xi_{r+1}} \\ &= \lim_{r \rightarrow \infty} \frac{\frac{1}{2} \sum_{n=1}^{\infty} (x_{r+n-1} - x_{r+n})}{\frac{1}{2} (x_r + x_{r+1})}\end{aligned}$$

\* (1)  $\phi'_+(0)$  denotes the right-hand derivative of  $\phi(x)$  at  $x = 0$ . Similarly,  $\phi'_-(0)$ . See Titchmarsh *Theory of Functions*, Oxford (1939), p. 354.

(2)  $x \rightarrow 0^+$  means  $x$  tending towards zero from the right. Similarly,  $x \rightarrow 0^-$ .

$$\begin{aligned}
&= \lim_{r \rightarrow \infty} \frac{1/2^{r+1}}{3/2^{r+2}} \\
&= \frac{2}{3}
\end{aligned}$$

And if we take

$$x = x_r,$$

the same metric density can similarly be shown to be

$$\begin{aligned}
&= \lim_{r \rightarrow \infty} \frac{1/2^{r+1}}{1/2^r} \\
&= \frac{1}{2} \neq \frac{2}{3}
\end{aligned}$$

Thus the required metric density at  $x=0$  does not exist though  $\phi'(0)$  exists

3 We shall now show that the existence of the same metric density at  $x=0$  is also not sufficient for the existence of  $\phi'(0)$ . Consider, for example, the step function defined below.—

In the interval  $(0, 1)$  define a set of points  $x_r$  such that  $x_r = 1/2^r$ ,  $r = 1, 2, 3$ . In each interval  $(x_{r+1}, x_r)$  choose a point  $\xi_{r+1}$  so that  $\xi_{r+1} = [(r+2)/(r+1)]x_{r+1}$ . Let then a function  $\phi(x)$  be defined in the interval  $(x_{r+1}, x_r)$  as follows.

$$\begin{aligned}
\phi(x) &= \frac{1}{2^r}, & x = x_r &= \frac{1}{2^r} \text{ with } r \text{ even,} \\
\phi(x) &= \frac{1}{2^{r-1}}, & x = x_r &= \frac{1}{2^r} \text{ with } r \text{ odd,} \\
\phi(x) &= \phi(x_{r+1}), & x_{r+1} &\leq x \leq \xi_{r+1} \\
\phi(x) &= \psi(x), & \xi_{r+1} &\leq x \leq x_r,
\end{aligned}$$

where  $\psi(x)$  is any monotone increasing and continuous function of  $x$ , with  $\psi(\xi_{r+1}) = \phi(\xi_{r+1})$  and  $\psi(x_r) = \phi(x_r)$ .

Let the function  $\phi(x)$  be defined as above for all positive integral values of  $r$  and let  $\phi(0)=0$ .

Obviously then  $\phi(x)$  is a monotone non-decreasing and continuous step function with  $\phi(0)=0$ . Also the interval  $(\xi_{r+1}, x_{r+1})$  is a line of invariability of  $\phi(x)$  for  $r = 1, 2, 3, \dots$ .

We shall now show that the metric density at  $x=0$  of the set of values of  $x$  corresponding to the lines of invariability of this function exists.

Whatever be  $x > 0$ , it must lie in some of the intervals  $(x_{r+1}, x_r)$ , and when it lies in  $(x_{r+1}, x_r)$  it must be either in  $(x_{r+1}, \xi_{r+1})$  or in  $(\xi_{r+1}, x_r)$ . Suppose we consider the former

i.e.,

$$x_{r+1} \leq x \leq \xi_{r+1}.$$

Then the metric density required

$$= \lim_{x \rightarrow 0} \frac{1}{x} \left[ (x - x_{r+1}) + \sum_{n=2}^{\infty} (\xi_{r+n} - x_{r+n}) \right]$$

which is easily seen to be  $\geq 0$  and

$$\leq \lim_{r \rightarrow \infty} \frac{1}{x_{r+1}} \sum_{n=1}^{\infty} (\xi_{r+n} - x_{r+n}),$$

which is

$$= \lim_{r \rightarrow \infty} 2^{r+1} \sum_{n=1}^{\infty} [1/(r+n) 2^{r+n}] \\ = 0$$

Similarly if  $x$  lies in the other interval,

$$\text{i.e.,} \quad \xi_{r+1} \leq x \leq x_r,$$

the metric density required

$$= \lim_{r \rightarrow \infty} \frac{1}{x} \sum_{n=1}^{\infty} (\xi_{r+n} - x_{r+n}),$$

which again  $\geq 0$ , and

$$\leq \lim_{r \rightarrow \infty} \frac{\sum_{n=1}^{\infty} [1/(r+n) 2^{r+n}]}{(r+2)/(r+1) 2^{r+1}},$$

which is

$$= 0.$$

Thus the required metric density exists and equals zero

But  $\phi'(0)$  does not exist, because  $\phi'_+(0)$  does not exist. For if we take

$$x = x_r = \frac{1}{2^r},$$

we have from the definition of  $\phi(x)$ ,

$$\frac{\phi(x_r)}{x_r} = \frac{1/2^r}{1/2^r} \text{ or } \frac{1/2^{r-1}}{1/2^r},$$

according as  $r$  is an even or odd integer respectively

Hence  $\frac{\phi(x_r)}{x_r}$  tends towards 1 or  $\sqrt{2}$  according as  $r$  tends towards  $\infty$  through even or odd integers respectively.

It follows, therefore, that  $\lim_{r \rightarrow \infty} \frac{\phi(x_r)}{x_r}$  does not exist, i.e.,  $\phi'_+(0)$  does not exist.

# LATTICE SUMS OF CUBIC CRYSTALS\*

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## INTRODUCTION

If  $a$  be the lattice constant of the undeformed cubic lattice then the distance  $r^{0l}$  of the point  $(l_1, l_2, l_3)$  from the point  $(0, 0, 0)$  is given by

$$(r^{0l})^2 = a^2 (l_1^2 + l_2^2 + l_3^2)$$

Here  $l_1, l_2, l_3$  are always integral, positive or negative

In order to explain the phenomena of stability, melting, tensile strength, etc we require lattice sums of the type

$$S_n^{(k_1, k_2, k_3)} = \sum_l' \frac{l_1^{2k_1} l_2^{2k_2} l_3^{2k_3}}{(l_1^2 + l_2^2 + l_3^2)^{n/2}},$$

the summation to extend over all possible positive and negative integral values of  $l_1, l_2, l_3$ . The dash over  $\Sigma$  denotes that  $l_1 = l_2 = l_3 = 0$  should be excepted.  $n$  is positive integral

Some of these sums have been calculated for certain values of  $n$  by the author (1940), who in collaboration with Prof Max Born (1940) has also developed a mathematical theory of these sums. Numerical calculations of the sum  $S_n^{(0)}$  have been published by Jones and Ingham (1925) with help of the use of Epstein Zeta functions. Our method, applicable to the general case, consisted in using Gamma and Theta functions and their transformations. Unfortunately these calculations are tedious for values of  $n$  greater than  $10 + 2(k_1 + k_2 + k_3)$ .

A method just suited for large values of  $n$  due to Born and Bormann (1920) is that in which lattice sums are added up to a certain stage by direct summation and the rest approximated by an integral.

The present paper consists of an improvement upon the latter method. We can calculate the upper and lower limits for the error committed in taking the approximation at any stage and thus we can obtain the lattice sums correct to any desired degree of accuracy.

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\* A summary of this paper was read at The Indian Science Congress, 1943



1. Let us consider the lattice sums

$$S_n^{(0)} = \sum_l' \frac{1}{(l_1^2 + l_2^2 + l_3^2)^{\frac{1}{2}n}}, \quad S_n^{(1)} = \sum_l' \frac{l_1^2}{(l_1^2 + l_2^2 + l_3^2)^{\frac{1}{2}n}}$$

$$S_n^{(2)} = \sum_l' \frac{l_1^4}{(l_1^2 + l_2^2 + l_3^2)^{\frac{1}{2}n}}; \quad S_n^{(1,1)} = \sum_l' \frac{l_1^2 l_2^2}{(l_1^2 + l_2^2 + l_3^2)^{\frac{1}{2}n}}$$

Between these quantities one has obviously the identities

$$3 S_n^{(1)} = S_{n-1}^{(0)}$$

$$3 S_n^{(2)} + 6 S_n^{(1,1)} = S_{n-1}^{(0)}$$

so that  $S^{(1)}$  and  $S^{(1,1)}$  can be expressed in terms of  $S^{(0)}$  and  $S^{(2)}$

2.  $S_n^{(0)}$  can be expressed as

$$S_n^{(0)} = \sum_{q=1}^{\infty} \frac{\nu_q^{(0)}}{q} = \sum_{q=1}^{p-1} \frac{\nu_q^{(0)}}{q^{\frac{1}{2}n}} + R_n^{(0)}(p) \quad (2.1)$$

where  $\nu_q^{(0)}$  is the number of neighbours at the distance  $q^{\frac{1}{2}}$  and

$$R_n^{(0)}(p) = \sum_{q=p}^{\infty} \frac{\nu_q^{(0)}}{q^{\frac{1}{2}n}} \quad (2.2)$$

$$\text{Similarly } S_n^{(2)} = \sum_{q=1}^{\infty} \frac{\nu_q^{(2)}}{q^{\frac{1}{2}n}} = \sum_{q=1}^{p-1} \frac{\nu_q^{(2)}}{q^{\frac{1}{2}n}} + R_n^{(2)}(p) \quad (2.3)$$

where  $\nu_q^{(2)}$  represents the sum of the fourth powers of  $l_i$  of all points at distance  $q^{\frac{1}{2}} = (l_1^2 + l_2^2 + l_3^2)^{\frac{1}{2}}$  from the origin and

$$R_n^{(2)}(p) = \sum_{q=p}^{\infty} \frac{\nu_q^{(2)}}{q^{\frac{1}{2}n}} \quad (2.4)$$

The following table gives the values of  $\nu_q^{(0)}$  and  $\nu_q^{(2)}$  for various possible values of  $q$  and corresponding  $l_1, l_2$  and  $l_3$ .

If  $q=1$ , obviously we can have

$$l_1 = \pm 1, l_2 = 0, l_3 = 0$$

$$\text{or } l_1 = 0, l_2 = \pm 1, l_3 = 0$$

$$\text{or } l_1 = 0, l_2 = 0, l_3 = \pm 1$$

and therefore  $\nu_1^{(0)}$  for  $q=1$  is 6 and  $\nu_1^{(2)}=2$ . We shall abbreviate all this into

saying that for  $q=1$ ,  $l_1, l_2, l_3$  are 1, 0, 0 and understand that cyclic as well as positive and negative values are to be taken for the  $l$ 's. Thus

	$q$	$l_1$	$l_2$	$l_3$	$\nu_1^0$	$\nu_1^2$	
$s$	1	0	0	1	6	2	
$sf$	2	0	1	1	12	8	
$sb$	3	1	1	1	8	8	
$sfb$	4	0	0	2	6	32	
$s$	5	0	1	2	24	136	
$sf$	6	1	1	2	24	144	
	7						
$sfb$	8	0	2	2	12	128	
$s$	9	{	1	2	24	264	
	0		0	3	6	162	
$sf$	10	0	1	3	24	656	
$sb$	11	1	1	3	24	664	
$sfb$	12	2	2	2	8	128	
$s$	13	0	2	3	24	776	
$sf$	14	1	2	3	48	1568	
	15						
$sfb$	16	0	0	4	6	512	
$s$	17	{	0	1	4	24	2056
	2		2	3	24	904	
$sf$	18	{	1	1	4	24	2064
	0		3	3	12	648	
$sb$	19	1	3	3	24	1304	

Here  $s$ ,  $f$ ,  $b$ , denote simple, face-centred and body-centred lattices respectively.

It will now be shown that

$$R_{\infty}^0(p) < \iiint_{x^2+y^2+z^2=p'} \frac{dxdydz}{(x^2+y^2+z^2)^{3/2}} + 3 \iint_{x^2+y^2=p''} \frac{dxdy}{(x^2+y^2)^{3/2}} + 6 \int_{x=\sqrt{p'''}} \frac{dx}{x^2} \quad (2.5)$$

but

$$> \iiint_{x^2+y^2+z^2=p} \frac{dxdydz}{(x^2+y^2+z^2)^{3/2}} - 3 \iint_{x^2+y^2=p} \frac{dxdy}{(x^2+y^2)^{3/2}} - 6 \int_{x=\sqrt{p}} \frac{dx}{x^2} \quad (2.6)$$

Here the three terms correspond to those lattice points for which none or one or two co-ordinates are zero and the values of lower limits  $p'$ ,  $p''$  and  $p'''$  have to be determined with the help of the above table. Any decomposition of  $p$  is one of the three types  $l^2+m^2+n^2$  (space),  $l^2+m^2$  (plane),  $l^2$  (axis), several of these may appear simultaneously. If one type or two do not occur for some  $p$ , we pick out the smallest of the numbers  $p+1$ ,  $p+2$ , . . . where the missing types occur, say  $p_1$  and  $p_2$ . Then in all these decompositions of  $p$ , and, if necessary, of  $p_1$  and  $p_2$ , we reduce  $l, m, n$  by unity and add their squares. The smallest amongst those of the three types are  $p'$ ,  $p''$  and  $p'''$ .

Consider the space divided into unit cubic cells by lines drawn at unit distances parallel to the axis,  $x, y$  and  $z$  axis being respectively parallel to the directions of  $l_1, l_2$  and  $l_3$ . Then corresponding to any one corner  $P_q$  of a cubic cell in space, there will be one, and only one, value of  $q$ . But corresponding to any value of  $q$  there will be  $\nu_j^{(0)}$  corners in space, all at a distance  $\sqrt{q}$  from the origin. With every corner not lying on a co-ordinate plane let us associate the cell of which it is the farthest corner from the origin. As a matter of fact no point lying on a co-ordinate plane can be the farthest corner of a cell, with such a point let us associate the square (or the unit segment of the axis if the point lies on an axis) of which it is the farthest corner (or far end). Fig. 1 illustrates this for the  $xy$  plane. For the point  $P_9$ ,  $q=3^2+2^2=13$ ; for  $q=5$  there are 8 points in the  $xy$  plane (24 points in space).

It is now obvious that in addition to the cubic cells we also require the unit squares on the co-ordinate planes and unit segments on co-ordinate axes so that every point corresponding to all possible values of  $q$  may have a cell or square or segment associated with it.

As  $P_j$  is the farthest corner of the cell (or square or segment) associated with it we have for all points  $x, y, z$  in the cell (or square or segment)

$$\frac{1}{q^{1/2}} \leq \frac{1}{(x' + y'^2 + z'^2)^{1/2}}$$

The nearest corner will be  $P_{j'}$  where

$$q' = (l-1)^2 + (m-1)^2 + (n-1)^2 \quad (2.7)$$

We now replace the sum  $\sum_{q=p}^{\infty} \frac{v_q^{(0)}}{q^{1/2}}$  by integrals over corresponding cells, squares and segments and get quite easily the inequality (2.5)

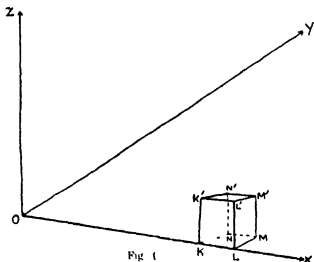


Fig. 1

To obtain the other inequality we associate this time with every corner that cell of which it is the nearest point. Every point on a co-ordinate plane can have two cells associated with it and every point on an axis four cells. This means that on associating one cell with every point we shall have some cells left unassociated, and therefore while integrating over the entire space we must exclude the integrals over the unassociated cells. The entire first layer on one side of every co-ordinate plane will remain unassociated so will a row of cells all along the length of every axis on the associated sides of the planes.

We can thus write

$$\sum_{q=p}^{\infty} \frac{v_q^{(0)}}{q^{1/2}} > \iiint \frac{dx \, dy \, dz}{(x^2 + y^2 + z^2)^{1/2}} - C \quad (2.8)$$

$$x^2 + y^2 + z^2 = p$$

where  $C$  is the integral over the excluded space.

Now from Fig 2 it is quite obvious that

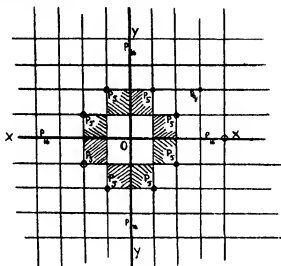


Fig 2

$$\frac{1}{(OK)^n} > \int_{x=OK}^{OL} \frac{dx}{x^n} > \int_{x=OK}^{OL} \int_{y=0}^1 \frac{dx dy}{(x^2 + y^2)^{n/2}} > \int_{x=OK}^{OL} \int_{y=0}^1 \int_{z=0}^1 \frac{dx dy dz}{(x^2 + y^2 + z^2)^{n/2}} \quad (2.9)$$

Using such inequalities to replace volume integrals over the excluded space, i.e., first layers of cells over co-ordinate planes and rows of cells along axes by surface integrals over the planes and line integrals over axes, respectively, we get instead of (2.8) the inequality (2.6)

The evaluation of these integrals is easy

$$\left. \begin{aligned} I_1(q) &= \int_{x^2+y^2+z^2=q}^{\infty} \int \int \frac{dx dy dz}{(x^2 + y^2 + z^2)^{n/2}} = \int_{\sqrt{q}}^{\infty} \frac{r^2 dr}{r^n} \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi \\ &= \frac{4\pi}{n-3} q^{\frac{1}{2}(n-3)} \\ I_2(q) &= 3 \int_{x^2+y^2=q}^{\infty} \int \frac{dx dy}{(x^2 + y^2)^{n/2}} = 3 \int_{\sqrt{q}}^{\infty} \frac{r dr}{r^n} \int_0^{2\pi} d\phi = \frac{6\pi}{n-2} q^{\frac{1}{2}(n-2)} \\ I_3(q) &= 6 \int_{\sqrt{q}}^{\infty} \frac{dx}{x^n} = \frac{6}{n-1} q^{\frac{1}{2}(n-1)} \end{aligned} \right\} \quad (2.10)$$

Then we get from (2.5), (2.6) and (2.10)

$$\begin{aligned} I_1(p') - I_1(p) + I_2(p'') + I_3(p''') &> S_n^0 - \left( \sum_{q=1}^{p-1} \frac{\nu_q^{(0)}}{q^{1/2}} + I_1(p) \right) \\ &> - \left( I_1(p) + I_2(p) \right) \end{aligned} \quad (2.11)$$

3 Next we consider  $S_n^{(2)}$  and the form expressed in (2.3). Associating cells, squares and lengths with  $P_q$ 's as before we get

$$\frac{l_3^4}{(l_1^2 + l_2^2 + l_3^2)^{1/2}} < \frac{(|r \cos \theta| + 1)^4}{r^n} \quad (3.1)$$

where  $r$  is any point in the cell, square or segment of which  $P_q$  ( $q = l_1^2 + l_2^2 + l_3^2$ ) is the farthest point, and  $|r \cos \theta|$  is the numerical value of  $r \cos \theta$ .

$$\text{Also} \quad \frac{l_1^4}{(l_1^2 + l_2^2 + l_3^2)^{1/2}} > \frac{(|r \cos \theta| - 1)^4}{r^n} \quad (3.2)$$

where  $r$  is any point in the cell, square or segment of which  $P_q$  is the nearest point.

On  $xy$  plane  $l_3 = 0$  and consequently also on  $x$  and  $y$  axes.

Replacing sums by integrals we obtain

$$\begin{aligned} J_1^+(p') - J_1^-(p) + J_2^+(p'') + J_3^+(p''') &> S_n^{(2)} - \left( \sum_{q=1}^{p-1} \frac{\nu_q^{(2)}}{q^{1/2}} + J_1^-(p) \right) \\ &> - \left( J_1^-(p) + J_2^-(p) \right) \end{aligned} \quad (3.3)$$

$$\begin{aligned} \text{where} \quad J_1^+(p') &= \int_{\sqrt{p}}^{\infty} \int_0^{\pi} \frac{(|r \cos \theta| + 1)^4}{r^n} r^2 \sin \theta \, dr \, d\theta \int_0^{2\pi} d\phi \\ &= 4\pi \left( \frac{1}{5(n-7)p'^{1/2}(n-7)} + \frac{1}{(n-6)p'^{1/2}(n-6)} + \frac{2}{(n-5)p'^{1/2}(n-5)} \right. \\ &\quad \left. + \frac{2}{(n-4)p'^{1/2}(n-4)} + \frac{1}{(n-3)p'^{1/2}(n-3)} \right) \end{aligned}$$

$$J_1^-(p) = \int_{\sqrt{p}}^{\infty} \int_0^{\pi} \frac{(|r \cos \theta| - 1)^4}{r^n} r^2 \sin \theta \, dr \, d\theta \int_0^{2\pi} d\phi$$

= the same as  $J_1^+(p)$  but with alternate terms positive and negative.

$$\begin{aligned}
 J_1^+(p'') &= 2 \int_{\sqrt{p''}}^{\infty} \int_0^{\pi} \frac{(|r \cos \theta| + 1)^4}{r^4} r dr d\theta \\
 &= -\frac{3\pi}{4(n-6)p''^{1/4(n-6)}} + \frac{3\pi}{3(n-5)p''^{1/4(n-5)}} + \frac{6\pi}{(n-4)p''^{1/4(n-4)}} \\
 &\quad + \frac{16}{(n-3)p''^{1/4(n-3)}} + \frac{2\pi}{(n-2)p''^{1/4(n-2)}} \\
 J_1^+(p''') &= 2 \int_{\sqrt{p'''}}^{\infty} \frac{(x+1)^4}{x^8} dx \\
 &= 2 \left[ \frac{1}{(n-5)p'''^{1/4(n-5)}} + \frac{4}{(n-4)p'''^{1/4(n-4)}} + \frac{6}{(n-3)p'''^{1/4(n-3)}} \right. \\
 &\quad \left. + \frac{4}{(n-2)p'''^{1/4(n-2)}} + \frac{1}{(n-1)p'''^{1/4(n-1)}} \right].
 \end{aligned}$$

$J_1^-(p)$  and  $J_2^-(p)$  are related to  $J_2^+(p)$  and  $J_1^+(p)$  respectively as  $J_1^-(p)$  is related to  $J_1^+(p)$

By properly choosing  $p$  we can make the difference of the two extreme sides of inequalities (2.11) and (3.8) as small as we like and then have approximately

$$\left. \begin{aligned}
 S_n^{(0)} &= \sum_{q=1}^{p-1} \frac{v_q^{(0)}}{q^{1/n}} + I_1(p) \\
 S_n^{(1)} &= \sum_{q=1}^{p-1} \frac{v_q^{(1)}}{q^{1/n}} + J_1^-(p)
 \end{aligned} \right\} \quad (3.4)$$

If  $p$  be large enough then quite a good approximation is obtained by considering only the first terms of  $I_1(p)$  and  $J_1^-(p)$  and we can then write

$$\left. \begin{aligned}
 S_n^{(0)} &= \sum_{q=1}^{p-1} \frac{v_q^{(0)}}{q^{1/n}} + \frac{4\pi}{(n-8)^{1/4(n-8)}} \\
 S_n^{(1)} &= \sum_{q=1}^{p-1} \frac{v_q^{(1)}}{q^{1/n}} + \frac{4\pi}{(n-7)^{1/4(n-7)}}
 \end{aligned} \right\} \quad (3.5)$$

The above calculation holds for the simple cubic lattice. For other two lattice types a modification has to be applied, namely, this. While the simple lattice has one cell per particle, face-centred has two and body-centred four cells per particle. Therefore it is easily seen that for the face-centred and body-centred lattice the remainder sums of the infinite series are one-half and one-fourth of those of the simple lattice.

4. So far we have discussed lattice sums of the type  $S_n^0, S_n^1, S_n^2, S_n^{1,1}$  only. The analysis can be extended to any  $S_n^{(k_1, k_2, k_3)}$  and it has not been given here for reasons of space.

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# INTENSITY CALCULATIONS FOR THE FINE STRUCTURE OF HYDROGENIC ATOMS PART I

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## 1. INTRODUCTORY

In their treatise on the Theory of Atomic Spectra (1935), Condon and Shortley having discussed the question of intensity in hydrogen spectra from the standpoint of Schrodinger mechanics write, "The relative strengths of the different doublets are not so simple since these (calculations) involve different radial integrals." They have suggested by this statement that calculations carried out so far by various authors\* beginning with Pauli (1933) and Schrodinger (1926) are defective in that they do not really lend any clue to relative strengths if the radial parts of the integrals in the intensity-matrix of the type  $\langle n l m j | P | n' l' m' j' \rangle$  be not exactly of identical value for both components of the doublet, and in the circumstances, these strengths must be assessed from spin consideration, that is to say, on the basis of Dirac's wave equations. The sum-rule for any Russell-Saunders multiplet as given by Ornstein, Burger and Dorgelo tells us that the strengths of a doublet would be proportional to the statistical weights of the components, and consequently the relative strengths of the lines  $^2S \rightarrow ^2P_{\frac{1}{2}}$  and  $^2S \rightarrow ^2P_{\frac{3}{2}}$  would be in the ratio 1:2 (there is one level in the S-state). This is not only true for hydrogen but for the S-P doublets of the alkalis. But departures have been noticed in the experimental ratio in Rb for the 2nd doublet, in Cs for the 2nd and 3rd doublets. This anomaly was tried to be solved by Fermi (1929) on the ground that there would be alteration in the spin-orbit interaction for the  $^2P_{\frac{1}{2}}$  and  $^2P_{\frac{3}{2}}$  series, and he suggested an altered radial function to explain the departure. But what actually would be the altered radial function? I think no body has yet attempted to find it out by actual calculation. I have attempted to show in this and the following papers, from the quantitative point of view, that inasmuch as the radial parts of the eigenfunctions in Dirac's equations for hydrogenic atoms for the levels  $j=l+\frac{1}{2}$  and  $j=l-\frac{1}{2}$  are different in the general case (Sec. 5), and the intensity matrix for S-P transitions with the same  $j$  value differs apparently from the matrix with different  $j$ 's, it is pure

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\*For literature, see Condon and Shortley, "Theory of Atomic Spectra" (1935), pp. 131-132

accident that we get identical values for the matrices, and as a matter of consequence, the relative strengths as 1 : 2 in the principal series of hydrogen. I have verified this ratio for the Lyman series of hydrogen in the present paper. The general method chalked out here can be utilised for intensity calculations for the Balmer series also (which will be taken up in Part II). I have utilised the eigenfunctions of Dirac's wave equations as expressed by me in terms of Sommerfeld's polynomial functions, essential properties of which have been studied in separate papers (Basu 1943*a*, 1943*b*).

## 2 STRENGTH OF A MULTIPLT

In a multiplet having  $(2j+1)$ -fold  $j$  values ( $j$  is two-fold for doublets, viz.,  $j=l+\frac{1}{2}$ ,  $l-\frac{1}{2}$ ) an energy level  $(n\ l\ j)$  is characterised by  $j$ , and is  $(2j+1)$ -fold degenerate in the absence of an external field, and the different states of the level have different  $m$ 's ( $j, j-1, \dots, -(j-1), -j$ ). Since the radiation emitted due to transitions between any state of  $j$  and another  $j'$  ( $j'=j+1, j, j-1$ ), and governed by  $\Delta l = \pm 1$ , form one component of the line, and the total intensity is the sum of the intensities of its components, we have in the case of dipole radiation

$$I(n\ l\ j, n'\ l'\ j') = N(n\ l\ j\ m) \frac{64\pi^4 \nu^4}{3c^3} \sum_m [(n\ l\ j\ m | e\mathbf{r} | n'\ l'\ j'\ m')]^2 \dots \quad (2'1)$$

where  $n' = m, m-1, m+1$ , and  $N(n\ l\ j\ m)$  is the number of atoms in the initial state  $(n\ l\ j\ m)$ , and  $\sum_m [(n\ l\ j\ m | e\mathbf{r} | n'\ l'\ j'\ m')]^2$  is the sum of spontaneous emission probabilities for several transitions  $(n\ l\ j\ m \rightarrow n'\ l'\ j'\ m')$ . Since the numbers of atoms in different states of the same level  $j$  are the same we have

$$N(n\ l\ j) = (2j+1) N(n\ l\ j\ m) \quad , \quad (2\ 2)$$

$$\text{and} \quad I(n\ l\ j, n'\ l'\ j') = N(n\ l\ j) h\nu A(n\ l\ j, n'\ l'\ j'), \quad (2\ 3)$$

where  $A(n\ l\ j, n'\ l'\ j')$  denotes the transition probability of Einstein for  $(n\ l\ j \rightarrow n'\ l'\ j')$ , that is to say,

$$A(n\ l\ j, n'\ l'\ j') = \frac{1}{2j+1} \frac{64\pi^4 e^2 \nu^3}{3hc^3} \sum_m [(n\ l\ j\ m | \mathbf{r} | n'\ l'\ j'\ m')]^2 \quad (2\ 4)$$

$$= \frac{1}{2j+1} S(n\ l\ j, n'\ l'\ j') \quad . \quad (2\ 5)$$

where  $S(n\ l\ j, n'\ l'\ j')$  is called the strength of the line  $(n\ l\ j \rightarrow n'\ l'\ j')$ .

We see then that the intensity (in ergs/sec per emitted atom) =  $S(n l j; n' l' j')/(2j+1)$ , and  $S$  is given by

$$S(n l j, n' l' j') = \frac{3^2 \pi^2 e^2 c^2}{3 \hbar} \sum_m [(n l j m | r | n' l' j' m')]^2 \quad (v = c\sigma) \quad (2'6)$$

We shall calculate  $S$  instead of  $I$  which is not symmetrical in the initial and final levels on account of the factor  $(2j+1)^{-1}$  associated with the initial level, whereas  $S$  is free from this asymmetry\*

### 3 SKETCH OF SOLUTIONS OF DIRAC'S EQUATIONS

The solutions of Dirac's 4-equations as given by Bethe (1933) are (note that  $\mu = \cos \theta$ ; and  $j_+ = l + \frac{1}{2}$ ,  $j_- = l - \frac{1}{2}$ )

$$\begin{aligned} \psi_1(n l m j_+) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l-m+\frac{1}{2})/(2l+3)} P_{l+1, m-\frac{1}{2}}(\mu) \exp i(m-\frac{1}{2})\phi_0 f_{nl}^+(r) \\ \psi_2(n l m j_+) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l+m+\frac{1}{2})/(2l+3)} P_{l+1, m+\frac{1}{2}}(\mu) \exp i(m+\frac{1}{2})\phi_0 f_{nl}^+(r) \\ \psi_3(n l m j_+) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l+m+\frac{1}{2})/(2l+1)} P_{l, m-\frac{1}{2}}(\mu) \exp i(m-\frac{1}{2})\phi_0 g_{nl}^+(r) \\ \psi_4(n l m j_+) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l-m+\frac{1}{2})/(2l+1)} P_{l, m+\frac{1}{2}}(\mu) \exp i(m+\frac{1}{2})\phi_0 g_{nl}^+(r) \\ \psi_1(n l m j_-) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l+m-\frac{1}{2})/(2l-1)} P_{l-1, m-\frac{1}{2}}(\mu) \exp i(m-\frac{1}{2})\phi_0 f_{nl}^-(r) \\ \psi_2(n l m j_-) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l-m-\frac{1}{2})/(2l-1)} P_{l-1, m+\frac{1}{2}}(\mu) \exp i(m+\frac{1}{2})\phi_0 f_{nl}^-(r) \\ \psi_3(n l m j_-) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l-m+\frac{1}{2})/(2l+1)} P_{l, m-\frac{1}{2}}(\mu) \exp i(m-\frac{1}{2})\phi_0 g_{nl}^-(r) \\ \psi_4(n l m j_-) &= \frac{1}{\sqrt{2\pi}} \sqrt{(l+m+\frac{1}{2})/(2l+1)} P_{l, m+\frac{1}{2}}(\mu) \exp i(m+\frac{1}{2})\phi_0 g_{nl}^-(r) \end{aligned} \quad (3.1)$$

where  $\psi(n l m j_+)$  denotes eigenfunction for  $j_+ (= l + \frac{1}{2})$  state,

$\psi(n l m j_-)$  denotes eigenfunction for  $j_- (= l - \frac{1}{2})$  state,

$$P_{lm}(\mu) = \left\{ \frac{1}{2} (2l+1) \frac{l-m!}{l+m!} \right\}^{\frac{1}{2}} P_l^m(\mu) \text{ (associated zonal harmonic),}$$

\*Oondon and Shortley, *loc. cit.*, Ch. 7, Sec. 7, p. 98.

$$F_{nl} = f_{nl}^+(x = -(j_+ + \frac{1}{2}) = -l-1), f_{nl}^-(x = (j_+ + \frac{1}{2}) = l)$$

$$G_{nl} = g_{nl}^+(x = -(j_+ + \frac{1}{2}) = -l-1), g_{nl}^-(x = (j_+ + \frac{1}{2}) = l) \quad (3.2)$$

and the radial functions in a combined form (Bose and Basu 1943) are given below :

$$\begin{aligned} rF_{nl} = & -\Delta_{nl} e^{-\frac{1}{2}\rho} \sqrt{1-\varepsilon} \rho^\gamma \left\{ \frac{n_r}{\sqrt{-x+\frac{aZ}{\sqrt{1-\varepsilon}}}} S_{2\gamma+1}^{n_r-1}(\rho) \right. \\ & \left. + \sqrt{-x+\frac{aZ}{\sqrt{1-\varepsilon}}} S_{2\gamma+1}^{n_r}(\rho) \right\} \\ rG_{nl} = & \Delta_{nl} e^{-\frac{1}{2}\rho} \sqrt{1+\varepsilon} \rho^\gamma \left\{ \frac{-n_r}{\sqrt{-x+\frac{aZ}{\sqrt{1-\varepsilon}}}} S_{2\gamma+1}^{n_r-1}(\rho) \right. \\ & \left. + \sqrt{-x+\frac{aZ}{\sqrt{1-\varepsilon}}} S_{2\gamma+1}^{n_r}(\rho) \right\} \quad (3.3) \end{aligned}$$

where

$$\varepsilon = E/m_0 c^2, \gamma = \sqrt{x^2 - a^2 Z^2}, a = \rho^2/c\hbar, \rho = 2\lambda r,$$

$$\lambda = \frac{m_0 c}{\hbar} \sqrt{1-\varepsilon^2}, n_r + \gamma = aZ/\sqrt{1-\varepsilon^2}, n \text{ (principal quantum number)}$$

$$= n_r \text{ (radial quantum number)} + |x| = n_r + j_+ + \frac{1}{2},$$

$$\Delta_{nl} \text{ (normalising factor)} = \frac{\sqrt{\Gamma(2\gamma+n_r+1)}}{\Gamma(2\gamma+1)\sqrt{n_r!}} \sqrt{\frac{\lambda}{2aZ}} \sqrt{1+\varepsilon^2} \quad (3.4)$$

and  $S_\nu^k(\rho)$  is a Sonine's polynomial of degree  $k$  and order  $\nu$  (non-integral)

The two-fold eigenvalues are

$$\begin{aligned} \varepsilon_+(n, j_+) = & 1 - \frac{1}{2} \frac{a^2 Z^2}{n^2} - \frac{1}{2} \frac{a^4 Z^4}{n^4} \left( \frac{1}{l+1} - \frac{3}{4n} \right) + \dots \\ \varepsilon_-(n, j_-) = & 1 - \frac{1}{2} \frac{a^2 Z^2}{n^2} - \frac{1}{2} \frac{a^4 Z^4}{n^4} \left( \frac{1}{l} - \frac{3}{4n} \right) + \dots \end{aligned} \quad (3.5)$$

We shall ignore in our calculations  $aZ, a^2 Z^2, \dots$  terms, as the value of  $a$  is  $1/137.2$ , provided  $Z$  is not very large (in the case of hydrogen it is 1). Again because  $F_{nl}$  involves a factor  $\sqrt{1-\varepsilon}$  which is  $\sim aZ$ , it is small in comparison with  $G_{nl}$  (the so-called "big component" of the radial function) and can safely be

neglected in our present case. Paying heed to these approximations we write down the following approximate values

$\lambda = Z/an \left( a = \hbar^2/m_0 e^2 \right)$ ;  $\sqrt{1-\varepsilon^2} = aZ/n$ ,  $\sqrt{1+\varepsilon} = \sqrt{2}$ ,  $x = -(j+\frac{1}{2})$  gives

$\gamma(j=l+\frac{1}{2}) = \gamma_1 = l+1-\frac{1}{2} \frac{a^2 Z^2}{l+\frac{1}{2}}$ ,  $\gamma(j=l-\frac{1}{2}) = \gamma_2 = l-\frac{1}{2} \frac{a^2 Z^2}{l}$ ,  $\gamma_1 - \gamma_2 - 1 = \frac{1}{2} \frac{a^2 Z^2}{l(l+\frac{1}{2})}$  ( $l > 0$ ) = a small +ve fraction, ( $l=0$  gives single state for S-level),  $x = + (j+\frac{1}{2})$  gives  $\gamma(j=l-\frac{1}{2}) = \gamma_1' = l-\frac{1}{2} \frac{a^2 Z^2}{l}$ ,  $\gamma(j=l+\frac{1}{2}) = \gamma_2' = l+1-\frac{1}{2} \frac{a^2 Z^2}{l+1}$ ,  $\gamma_1' - \gamma_2' - 1 = \frac{1}{2} \frac{a^2 Z^2}{l(l-1)}$  ( $l > 1$ ) = a small +ve fraction.

$$\left. \begin{aligned} \Delta_{n,l}^{+} (j=l+\frac{1}{2}) &= \frac{1}{\sqrt{2}} \frac{1}{n} \left( \frac{Z}{a} \right)^{\frac{1}{2}} \frac{\sqrt{2\gamma_1 + n - l}}{\Gamma(2\gamma_1 + 1) \sqrt{n-l-1!}} \quad (n_r = n-l-1) \\ \Delta_{n,l-1}^{-} (j=l-\frac{1}{2}) &= \frac{1}{\sqrt{2}} \frac{1}{n'} \left( \frac{Z}{a} \right)^{\frac{1}{2}} \frac{\sqrt{2\gamma_1' + n' - l + 1}}{\Gamma(2\gamma_1' + 1) \sqrt{n'-l!}} \quad (n_r' = n'-l) \end{aligned} \right\} \quad (36)$$

The 'a' given above is the radius of the innermost Bohr H-atom, which is taken as unity in atomic (Hartree) units

#### 4 SELECTION RULES AND INTENSITY MATRICES

Since  $(n | \varepsilon r | n')$  is the matrix defining the moment of electrical density in space for the transition  $n \rightarrow n'$  and the dipole radiation for the transition is isotropic and unpolarised it will be independent of the angular co-ordinates. At first we shall calculate the matrix elements

$$(n | l m f | x | n' l' m' f'), (n | l m f | x + Jy | n' l' m' f') \quad (J = \pm i) \quad (4.1)$$

remembering  $x = r \cos \theta$ ,  $x + Jy = r \sin \theta e^{J\phi}$ ,

$$\frac{1}{2\pi} \int_0^{2\pi} \exp i (m - m') \phi d\phi = \delta_{mm'}, \quad \int_{-1}^1 P_l'(\mu) P_l(\mu) d\mu = \delta_{l'l}, \quad (4.2)$$

and the following sequence relations

$$\begin{aligned} \cos \theta P_l &= \sqrt{\frac{(l+1)^2 - m^2}{(2l+3)(2l+1)}} P_{l+1} = + \sqrt{\frac{l^2 - m^2}{(2l+1)(2l-1)}} P_{l-1} \\ \sin \theta P_l &= - \sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} P_{l+1} = -1 + \sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}} P_{l-1} = -1, \\ \sin \theta P_l &= \sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} P_{l+1} = +1 - \sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}} P_{l-1} = +1 \end{aligned} \quad (4.3)$$

We have

$$(n \ l \ m \ j \mid x \mid n' \ l' \ m' \ j') = \int_0^\infty \int_{-1}^1 \int_0^{2\pi} \{\psi_{n' l' m'}^* (n l m j) \psi_{n' l' m' j'} + 3 \text{ others}\} r^3 \cos \theta d\mu dr d\phi \quad (4.4)$$

$$(n \ l \ m \ j \mid x + jy \mid n' \ l' \ m' \ j') = \int_0^\infty \int_{-1}^1 \int_0^{2\pi} \{\psi_{n' l' m'}^* (n l m j) \psi_{n' l' m' j'} + 3 \text{ others}\} e^{i\phi} r^3 \sin \theta d\mu dr d\phi \quad (4.5)$$

and in order that we may get contributions to the matrices we will have the following selection rules

$$m = m' \ (\Delta m = 0), \quad l = l' \pm 1 \ (\Delta l = \pm 1) \quad \text{from (4.4)}$$

$$\text{and an additional rule} \quad \Delta m = \pm 1 \quad \text{from (4.5)}$$

We give below the results of our calculations in a tabular form, noting  $j_+ - j_- = 1$

Matrices	Values	$(\Delta j \ \Delta l \ \Delta m)$
$(n \ l \ m \ j_+ \mid x \mid n' \ l+1 \ m \ j_+ + 1)$	$\frac{\sqrt{(l+\frac{1}{2})^2 - m^2}}{2l+3} \left( R_{n'l_+}^{n'l+1,+} \right)$	1 1 0
$(n \ l \ m \ j_+ \mid x \mid n' \ l-1 \ m \ j_+ - 1)$	$\frac{\sqrt{(l-\frac{1}{2})^2 - m^2}}{2l+1} \left( R_{n'l_+}^{n'l-1,+} \right)$	-1 -1 0
$(n \ l \ m \ j_- \mid x \mid n' \ l+1 \ m \ j_- + 1)$	$\frac{\sqrt{(l+\frac{1}{2})^2 - m^2}}{2l+1} \left( R_{n'l_-}^{n'l+1,-} \right)$	1 1 0
$(n \ l \ m \ j_- \mid x \mid n' \ l-1 \ m \ j_- - 1)$	$\frac{\sqrt{(l-\frac{1}{2})^2 - m^2}}{2l+1} \left( R_{n'l_-}^{n'l-1,-} \right)$	-1 -1 0
$(n \ l \ m \ j_+ \mid x \mid n' \ l+1 \ m \ j_- + 1)$	$\frac{2m}{(2l+1)(2l+3)} \left( R_{n'l_+}^{n'l+1,-} \right)$	0 1 0
$(n \ l \ m \ j_- \mid x \mid n' \ l-1 \ m \ j_+ - 1)$	$\frac{2m}{(2l-1)(2l+1)} \left( R_{n'l_-}^{n'l-1,+} \right)$	0 -1 0
$(n \ l \ m \ j_+ \mid x + iy \mid n' \ l+1 \ m+1 \ j_+ + 1)$	$\frac{\sqrt{(l+m+\frac{1}{2})(l+m+\frac{3}{2})}}{2l+3} \left( R_{n'l_+}^{n'l+1,+} \right)$	1 1 1
$(n \ l \ m \ j_+ \mid x + iy \mid n' \ l-1 \ m+1 \ j_+ - 1)$	$-\frac{\sqrt{(l-m-\frac{1}{2})(l-m+\frac{1}{2})}}{2l+1} \left( R_{n'l_+}^{n'l-1,+} \right)$	-1 -1 1
$(n \ l \ m \ j_+ \mid x - iy \mid n' \ l+1 \ m-1 \ j_+ + 1)$	$-\frac{\sqrt{(l-m+\frac{1}{2})(l-m+\frac{3}{2})}}{2l+3} \left( R_{n'l_+}^{n'l+1,+} \right)$	1 1 -1
$(n \ l \ m \ j_+ \mid x - iy \mid n' \ l-1 \ m-1 \ j_+ - 1)$	$\frac{\sqrt{(l+m-\frac{1}{2})(l+m+\frac{1}{2})}}{2l+1} \left( R_{n'l_+}^{n'l-1,+} \right)$	-1 -1 -1

$$\begin{aligned}
(n \ l \ m \ j_- | x+iy | n' l+1 \ m+1 \ j_-+1) &= \frac{\sqrt{(l+m+\frac{1}{2})(l+m+\frac{3}{2})}}{2l+1} \left( R_{n'l_-}^{n'l+1} \right) (1 \ 1 \ 1) \\
(n \ l \ m \ j_- | x+iy | n' l-1 \ m+1 \ j_- -1) &= \frac{\sqrt{(l-m-\frac{1}{2})(l-m-\frac{3}{2})}}{2l-1} \left( R_{n'l_-}^{n'l-1} \right) (-1 \ -1 \ 1) \\
(n \ l \ m \ j_- | x-iy | n' l+1 \ m-1 \ j_-+1) &= \frac{\sqrt{(l-m+\frac{1}{2})(l-m+\frac{3}{2})}}{2l+1} \left( R_{n'l_-}^{n'l+1} \right) (1 \ 1 \ -1) \\
(n \ l \ m \ j_- | x-iy | n' l-1 \ m-1 \ j_- -1) &= \frac{\sqrt{(l+m-\frac{1}{2})(l+m-\frac{3}{2})}}{2l-1} \left( R_{n'l_-}^{n'l-1} \right) (-1 \ -1 \ -1) \\
(n \ l \ m \ j_+ | x+iy | n' l+1 \ m-1 \ j_-+1) &= 2 \frac{\sqrt{(l-m+\frac{1}{2})(l+m+\frac{1}{2})}}{(2l+1)(2l+3)} \left( R_{n'l_+}^{n'l+1} \right) (0 \ 1 \ -1) \\
(n \ l \ m \ j_+ | x-iy | n' l+1 \ m+1 \ j_-+1) &= 2 \frac{\sqrt{(l-m+\frac{1}{2})(l+m+\frac{3}{2})}}{(2l+1)(2l+3)} \left( R_{n'l_+}^{n'l+1} \right) (0 \ 1 \ 1) \\
(n \ l \ m \ j_- | x+iy | n' l-1 \ m-1 \ j_+ -1) &= 2 \frac{\sqrt{(l-m+\frac{1}{2})(l+m-\frac{1}{2})}}{(2l+1)(2l-1)} \left( R_{n'l_-}^{n'l-1} \right) (0 \ -1 \ -1) \\
(n \ l \ m \ j_- | x-iy | n' l-1 \ m+1 \ j_+ -1) &= 2 \frac{\sqrt{(l+m+\frac{1}{2})(l-m-\frac{1}{2})}}{(2l+1)(2l-1)} \left( R_{n'l_-}^{n'l-1} \right) (0 \ -1 \ 1)
\end{aligned}$$

where

$$\left( R_{n'l_+}^{n'l+1} \right) = \int_0^\infty r^3 \left( f_{n'l}^+ f_{n'l}^+ + g_{n'l}^+ g_{n'l}^+ \right) dr \sim \int_0^\infty r^3 g_{n'l}^+ g_{n'l}^+ dr, \quad (\alpha Z \ll 1)$$

$$\left( R_{n'l_-}^{n'l-1} \right) = \int_0^\infty r^3 \left( f_{n'l}^- f_{n'l}^- + g_{n'l}^- g_{n'l}^- \right) dr \sim \int_0^\infty r^3 g_{n'l}^- g_{n'l}^- dr,$$

$$\left( R_{n'l_+}^{n'l-1} \right) = \int_0^\infty r^3 \left( f_{n'l}^+ f_{n'l}^- + g_{n'l}^+ g_{n'l}^- \right) dr \sim \int_0^\infty r^3 g_{n'l}^+ g_{n'l}^- dr,$$

$$\left( R_{n'l_-}^{n'l+1} \right) = \int_0^\infty r^3 \left( f_{n'l}^- f_{n'l}^+ + g_{n'l}^- g_{n'l}^+ \right) dr \sim \int_0^\infty r^3 g_{n'l}^- g_{n'l}^+ dr$$

Working out the summations for all the states of  $m'$  ( $\pm \frac{1}{2}, m, m+1, m-1$ ) according to the well-known rule

$$\sum_{m'} [(n \ l \ j | r | n' l \pm 1 \ j')]^2 = [(n \ l \ m \ j | x | n' l \pm 1 \ m \ j')]^2 +$$

$\frac{1}{2}[(n \ l \ m \ j | x + iy | n' l \pm 1 \ m + 1 \ j')]^2 + \frac{1}{2}[(n \ l \ m \ | x - iy | n' l + 1 \ m - 1 \ j')]^2$ ,  
we derive the following

$$\sum_m [(n \ l \ j_+ | r | n' l + 1 \ j_+ + 1)]^2 = \frac{l+2}{2l+3} \left( R_{nl_+}^{n'l+1} \right)^2, \quad (\Delta j = 1, \Delta l = 1)$$

$$\sum_m [(n \ l \ j_+ | r | n' l - 1 \ j_+ - 1)]^2 = \frac{l}{2l+1} \left( R_{nl_+}^{n'l-1} \right)^2, \quad (\Delta j = 0, \Delta l = -1)$$

$$\sum_m [(n \ l \ j_- | r | n' l + 1 \ j_- + 1)]^2 = \frac{l+1}{2l+1} \left( R_{nl_-}^{n'l+1} \right)^2, \quad (\Delta j = 1, \Delta l = 1)$$

$$\sum_m [(n \ l \ j_- | r | n' l - 1 \ j_- - 1)]^2 = \frac{l-1}{2l-1} \left( R_{nl_-}^{n'l-1} \right)^2, \quad (\Delta j = -1, \Delta l = -1)$$

$$\sum_m [(n \ l \ j_+ | r | n' l + 1 \ j_- + 1)]^2 = \frac{1}{(2l+1)(2l+3)} \left( R_{nl_+}^{n'l+1} \right)^2, \quad (\Delta j = 0, \Delta l = 1)$$

$$\sum_m [(n \ l \ j_- | r | n' l - 1 \ j_+ - 1)]^2 = \frac{1}{(2l-1)(2l+1)} \left( R_{nl_-}^{n'l-1} \right)^2, \quad (\Delta j = 0, \Delta l = -1)$$

(4.6)

## 5 EXPRESSIONS FOR THE $R$ 's

Written explicitly .

$$[\gamma_1 = \sqrt{(l+1)^2 - \alpha^2 Z^2}, \quad \gamma_2 = \sqrt{l^2 - \alpha^2 Z^2}]$$

$$\left( R_{nl_+}^{n'l-1} \right) =$$

$$\Delta_{nl}^+ \Delta_{n'l-1}^+ \sqrt{1 + \epsilon_+(nl)} \sqrt{1 + \epsilon_+(n'l-1)} \int_0^\infty (2\lambda_1 r)^{\gamma_1} (2\lambda_2 r)^{\gamma_2} e^{-\frac{Z}{a} \left( \frac{1}{n} + \frac{1}{n'} \right) r} \times$$

$$\left\{ -\frac{n-l-1}{\sqrt{l+1+\frac{\alpha Z}{\sqrt{1-\epsilon_+^2(nl)}}}} S_{2\gamma_1+1}^{n-l-2} \left( \frac{2Zr}{na} \right) + \sqrt{l+1+\frac{\alpha Z}{\sqrt{1-\epsilon_+^2(nl)}}} S_{2\gamma_1+1}^{n-l-1} \left( \frac{2Zr}{na} \right) \right\} \times$$

$$\left\{ -\frac{n'-l}{\sqrt{l+\frac{\alpha Z}{\sqrt{1-\epsilon_+^2(n'l-1)}}}} S_{2\gamma_1+1}^{n'-l-1} \left( \frac{2Zr}{na} \right) + \sqrt{l+\frac{\alpha Z}{\sqrt{1-\epsilon_+^2(n'l-1)}}} S_{2\gamma_1+1}^{n'-l} \left( \frac{2Zr}{na} \right) \right\} r dr$$

... (5.1)





$$\{\text{VII}\} = \int_0^{\infty} r^{\gamma'+\gamma_s'+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma_s'+1}^{n-l-1}\left(\frac{2Zr}{n}\right) S_{2\gamma_s'+1}^{n'-l+1}\left(\frac{2Zr}{n'}\right) dr,$$

$$\{\text{VIII}\} = \int_0^{\infty} r^{\gamma'+\gamma_s'+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma_s'+1}^{n-l}\left(\frac{2Zr}{n}\right) S_{2\gamma_s'+1}^{n'-l}\left(\frac{2Zr}{n'}\right) dr,$$

$$\begin{aligned} \left(R_{nl+}^{n'+l-1}\right) = a \frac{Z^{2\gamma+1} 2^{2\gamma}}{(nn')^{\gamma+1}} \sqrt{\frac{n+l}{n-l-1} \frac{n'+l+1}{n'-l-1}} & \left[ (n-l-1) \{\text{IX}-\text{XI}\} \right. \\ & \left. + (n+l+1) \{\text{X}-\text{XII}\} \right], \quad [\gamma = \sqrt{(l+1)^2 - \alpha^2 Z^2}], \end{aligned} \quad (5.4)$$

where

$$\{\text{IX}\} = \int_0^{\infty} r^{2\gamma+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma+1}^{n-l-2}\left(\frac{2Zr}{n}\right) S_{2\gamma+1}^{n'-l-2}\left(\frac{2Zr}{n'}\right) dr,$$

$$\{\text{X}\} = \int_0^{\infty} r^{2\gamma+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma+1}^{n-l-2}\left(\frac{2Zr}{n}\right) S_{2\gamma+1}^{n'-l-1}\left(\frac{2Zr}{n'}\right) dr,$$

$$\{\text{XI}\} = \int_0^{\infty} r^{2\gamma+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma+1}^{n-l-1}\left(\frac{2Zr}{n}\right) S_{2\gamma+1}^{n'-l-1}\left(\frac{2Zr}{n'}\right) dr,$$

$$\{\text{XII}\} = \int_0^{\infty} r^{2\gamma+1} e^{-Z\left(\frac{1}{n} + \frac{1}{n'}\right)r} S_{2\gamma+1}^{n-l+1}\left(\frac{2Zr}{n}\right) S_{2\gamma+1}^{n'-l-2}\left(\frac{2Zr}{n'}\right) dr$$

Evaluation of these integrals has been carried out in Appendices A and B ignoring the constant factor 'a'. In the expressions for S we will get  $3\pi^2 \pi^2 \sigma^2 (e^2 a^2)/3\hbar$  times the values given in the appendices. In the atomic unit ( $ea$ ) is taken to be unity and the wave number  $\sigma$ , which is given by  $\sigma = -Ry Z^2/n^2$ , where  $Ry$  stands for the Rydberg constant  $m_0 e^4/4\pi\hbar^2 c$  is calculated taking  $Ry$  to be unity.

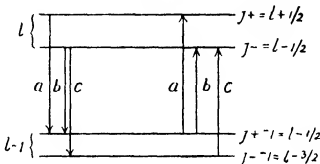
## 6 CALCULATION OF RELATIVE STRENGTHS

With the help of results (A. 1), (A. 2) and (A. 6) of Appendix A the matrices given in (4.6) can be worked out in the general cases.

Let us consider a general case of transition, for the doublet spectra of hydrogen, from the two levels  $(n, l, j_+)$  to  $(n', l-1, j_+-1)$ ,  $(n', l-1, j_--1)$ .

From the selection rules we get only three lines in general, viz.,  $a (n l j_+ \rightarrow n' l-1 j_+-1)$ ,  $b (n l j_- \rightarrow n' l-1 j_+-1)$ ,  $c (n l j_- \rightarrow n' l-1 j_--1)$ . From (2.4) and (4.6) we get the strengths  $S(a)$ ,  $S(b)$ ,  $S(c)$ , barring the constant factor

$$(32\pi^2 \sigma^2 e^2 a^2 / 3 \hbar Z^2),$$



according to the rule of Ornstein-Dorgelo :

$$S(a) = (2j_+ + 1) \frac{l}{2l+1} \left( R_{nl+}^{n'l-1+} \right)^2 \quad . \quad . \quad . \quad (6.1)$$

$$S(b) + S(c) = (2j_- + 1) \left\{ \frac{1}{(2l-1)(2l+1)} \left( R_{nl-}^{n'l-1+} \right)^2 + \frac{l-1}{2l-1} \left( R_{nl-}^{n'l-1-} \right)^2 \right\} \quad (6.2)$$

Evidently, in the above, the initial state is  $l$ -state (the lines in the fig are indicated to the left). Again, if the initial state be the  $(l-1)$ -state, we get, according to the same rule (see lines to the right)

$$S(a) + S(b) = (2j_+ - 1) \left\{ \frac{l+1}{2l+1} \left( R_{nl+}^{n'l+} \right)^2 + \frac{1}{(2l-1)(2l+1)} \left( R_{nl-1-}^{n'l+} \right)^2 \right\} \quad (6.3)$$

$$S(c) = (2j_- - 1) \frac{l}{2l-1} \left( R_{nl-1-}^{n'l-} \right)^2 \quad . \quad . \quad . \quad (6.4)$$

Taking for granted that the  $R$ 's have identical values in (6.1), (6.2), (6.3), (6.4), easy calculations give after simplifications :

$$\frac{S(b) + S(c)}{S(a)} = \frac{l}{l+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.5)$$

$$\text{and} \quad \frac{S(a) + S(b)}{S(c)} = \frac{l}{l-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.6)$$

Adding 1 to both sides of (6.5) and (6.6) we get

$$S(c)/S(a) = (l-1) (2l+1)/(l+1) (2l-1) \quad . \quad . \quad . \quad . \quad (6.7)$$

$$S(b)/S(a) = 1/(l+1) (2l-1) \quad . \quad . \quad . \quad . \quad (6.8)$$

The last two equations yield the result :

$$S(a) : S(b) : S(c) = (l+1) (2l-1) : 1 : (l-1) (2l+1) \quad . \quad . \quad . \quad (6.9)$$

In particular, we know when  $l=1$ , (line  $c$  is absent, there is no doubling of the S-state) and for the Lyman series, the R's are identical (according to our calculations given in Appendix B) so that we get

$$S(a)/S(b)=2/1, \text{ or, } sp_1 \cdot sp_1 \quad 2 \quad 1 \quad (6.10)$$

Similarly, by putting  $l=2, l=3$  we derive

$$pd\text{-transitions} \quad p_1d_1 \cdot p_1d_1 \cdot p_1d_1 = 9 \quad 1 \quad 5$$

$$df\text{-transitions} \quad d_1f_1 \quad d_1f_1 \cdot d_1f_1 = 20 \quad 1 \quad 14$$

This rule does not hold true if the R's be different. In the case of Rb and Cs, for instance, we may remark *a priori* that the departures noticed in experiments will be quite consistent with theoretical results (although it is premature to verify the experimental results at present). The electron compositions for those alkalis are

$$\text{Rb (Z=37)} \quad (1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^4 4p^6) 5s$$

$$\text{Cs (Z=55)} \quad (1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^4 4p^6 4d^{10} 5s^2 5p^6) 6s$$

The s-levels start with principal quantum numbers  $n'=5$  and  $n'=6$  respectively; and we have to calculate for Rb  $5s \rightarrow np_1, np_1$  ( $n=5, 6$ , for the 1st, 2nd, doublets), and for Cs:  $6s \rightarrow np_1, np_1$  ( $n=6, 7$ , for the 1st, 2nd, .. doublets) for their principal series. Since in these cases  $\alpha Z$  is of the order  $\sim 1/3.7$  and  $\sim 1/3.5$  which are not negligible quantities in comparison with unity, we will have to evaluate the radial parts of the eigen-functions without ignoring the  $\alpha Z$  terms. This will possibly explain the departures from experimental values.

For the Lyman series the radial functions  $(R_{n,l}^{10+}), (R_{n,l}^{10-}), (R_{n,l}^{10})$  and  $(R_{n,l}^{10+})$  have the same value (See Appendix B, Eqs. B 3, B 11, B 15)

## APPENDIX A

In Papers I and II the following integrals have been established.

$$\begin{aligned} \{A\} &= \int_0^\infty x^p e^{-(\lambda_1 + \lambda_2)x} S_\lambda^m(2\lambda_1 x) S_\mu^m(2\lambda_2 x) dx \quad (p+1 \geq \lambda \geq \mu) \\ &= \frac{n! m! \Gamma(\lambda) \Gamma(\mu)}{(\lambda_1 + \lambda_2)^{p+1} \Gamma(\lambda + n) \Gamma(\mu + m)} \sum_{r=0}^n \sum_{r'=0}^m \sum_{v=0}^{m \leq n} (-1)^{m+n+r'-v} \left( \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \right)^{r+r'-2v} \times \\ &\quad \left( \frac{p+1-\lambda}{n-v} \right) \left( \frac{p+1-\mu}{m-v'} \right) \frac{\Gamma(p+1+r+v-v)}{v-v! v'-v! v!} \quad (A.1) \end{aligned}$$

$$\begin{aligned}
[B] &= \int_0^\infty x^{\gamma_1 + \gamma_2 + 1} e^{-(\lambda_1 + \lambda_2)x} S_{2\gamma_1 + 1}^n(2\lambda_1 x) S_{2\gamma_2 + 1}^m(2\lambda_2 x) dx \quad (\gamma_1 - 1 - \gamma_2 = a + \text{ve frac-} \\
&\hspace{15em} \text{tion} \ll 1) \\
&= \frac{n! m! \Gamma(2\gamma_1 + 1) \Gamma(2\gamma_2 + 1)}{(\lambda_1 + \lambda_2)^{\gamma_1 + \gamma_2 + 2} \Gamma(2\gamma_1 + n + 1) \Gamma(-\gamma_2 + m + 1) \Gamma(\gamma_1 - \gamma_2 - 1)} \sum_{r=0}^n \sum_{r'=0}^m \sum_{r''=0}^{m-r'} (-)^{m+r+r''} \\
&\times \left( \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \right)^{r+r'-2r''} \binom{\gamma_1 + 1 - \gamma_2}{m - r'} \frac{\Gamma(\gamma_1 - \gamma_2 - 1 + n - r) \Gamma(\gamma_1 + \gamma_2 + 2 + r + r' - r'')}{n - r! r' - r''! r''!} \quad (A.2)
\end{aligned}$$

Integrals in (5.2) and (5.3) can be evaluated with the help of (A.2), and the integrals in (5.4) can be evaluated with the help of (A.1). In the former case,  $\gamma_1$  and  $\gamma_2$  being equal (each =  $\gamma$ ), the contribution to the series

$$\binom{\gamma_1 + 1 - \gamma_2}{m - r'} = \binom{1}{m - r'}$$

comes from  $r' = m$  and  $r' = m - 1$  only, and for each of these values of  $r'$  the contribution is 1. For ordinary calculations  $m$  generally takes the values 0, 1, 2,

So we require to evaluate a simpler integral of the type given below:

$$[C] = \int_0^\infty x^\rho e^{-(\lambda_1 + \lambda_2)x} S_\lambda^n(2\lambda_1 x) dx \quad (A.3)$$

$$\text{Since } \frac{\exp(-2\lambda_1 x t / (1-t))}{(1-t)^\lambda} = \sum_{r=0}^n \frac{t^r}{r!} \frac{\Gamma(\lambda + n)}{\Gamma(\lambda)} S_\lambda^n(2\lambda_1 x), \quad (\text{See, I})$$

multiply both sides by  $x^\rho \exp(-(\lambda_1 + \lambda_2)x$  and integrate between 0 and  $\infty$ .

$$\sum_{r=0}^n \frac{t^r}{r!} \frac{\Gamma(\lambda + n)}{\Gamma(\lambda)} \int_0^\infty x^\rho e^{-(\lambda_1 + \lambda_2)x} S_\lambda^n(2\lambda_1 x) dx = \frac{1}{(1-t)^\lambda} \int_0^\infty x^\rho e^{-\Lambda x} dx, \quad (A.4)$$

where  $\Lambda = (\lambda_1 + \lambda_2) (1 + \theta t) / (1 - t)$  and  $\theta = (\lambda_1 - \lambda_2) / (\lambda_1 + \lambda_2)$

$$\text{Right-hand member} = \frac{1}{(1-t)^\lambda} \cdot \frac{\Gamma(p+1)}{\Delta^{p+1}} = \frac{\Gamma(p+1)}{(\lambda_1 + \lambda_2)^{p+1} (1-t)^{p+1-\lambda} (1+\theta t)^{p-1}} \quad (A.5)$$

$$\therefore [C] = \frac{n! \Gamma(\lambda)}{\Gamma(\lambda + n)} \times \{\text{coeff of } t^n \text{ in the expansion of (A.5)}\}$$

$$= \frac{n! \Gamma(\lambda)}{\Gamma(\lambda + n)} \cdot \frac{\Gamma(p+1)}{(\lambda_1 + \lambda_2)^{p+1}} \sum_{r_1, r_2} (-)^{r_1} \binom{p+1-\lambda}{r_1} \frac{\Gamma(p+r_2+1)}{\Gamma(p+1)r_2!} \theta^{r_1+r_2}$$

If  $r_1 + r_2 = n$ , then putting  $r_1 = \tau$  say, we derive :

$$[C] = \frac{n! \Gamma(\lambda)}{\Gamma(\lambda + n) (\lambda_1 + \lambda_2)^{n+1}} \sum_{\tau=0}^n (-)^{n-\tau} \binom{p+1-\lambda}{n-\tau} \frac{\Gamma(p+\tau+1)}{\tau!} \left( \frac{\lambda_1 - \lambda_2}{\lambda_1 + \lambda_2} \right)^\tau \quad (A 6)$$

## APPENDIX B

Making  $\gamma_1 = l+1$ ,  $\gamma_2 = l$ , (5.2) becomes

$$\begin{aligned} \left( R_{n'l+}^{n-l+1} \right) &= \frac{Z^{l+1} 2^{l+1}}{n^{l+1} n'^{l+1}} \sqrt{\frac{n+l+1}{n-l-1}} \frac{n'+l}{n'-l} \times \\ &\left\{ \frac{(n-l-1)(n'-l)}{\sqrt{(n+l+1)(n'+l)}} \{I'\} + \sqrt{(n+l+1)(n'+l)} \{II'\} - \right. \\ &\left. \frac{(n-l-1)\sqrt{n'+l}}{\sqrt{n+l+1}} \{III'\} - \frac{(n'-l)\sqrt{n+l+1}}{\sqrt{n'+l}} \{IV'\} \right\} \quad (B.1) \end{aligned}$$

In the above put  $l=1$   $n' \ll 1$  and get

$$\left( R_{n1+}^{10+} \right) = \frac{Z^4 2^4 \sqrt{(n+1)n(n-1)}}{4! 2! n^5} [(n+2)\{II'\} - (n-2)\{III'\}] \quad (B 2)$$

where

$$\begin{aligned} \{II'\} &= \int_0^\infty r^{\gamma_1+\gamma_2+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1+1}^{n-2} \left( \frac{2Zr}{n} \right) dr = \frac{4!}{Z^5} \left( \frac{n}{n+1} \right)^5 \left( \frac{n-1}{n+1} \right)^{n-2} \\ &\quad \gamma_1 \rightarrow 2 \quad 0 \\ &\quad \gamma_2 \rightarrow 1 \end{aligned} \quad (\text{from A 5}) \quad (B 3)$$

$$\begin{aligned} \{III'\} &= \int_0^\infty r^{\gamma_1+\gamma_2+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1+1}^{n-3} \left( \frac{2Zr}{n} \right) dr = \frac{4!}{Z^5} \left( \frac{n}{n+1} \right)^5 \left( \frac{n-1}{n+1} \right)^{n-3} \\ &\quad \gamma_1 \rightarrow 2 \quad 0 \\ &\quad \gamma_2 \rightarrow 1 \end{aligned} \quad (B 4)$$

$$(n+2) \{II'\} - (n-2) \{III'\} = \frac{4!}{Z^5} 2n^4 \frac{(n-1)^{n-2}}{(n+1)^{n+1}}.$$

Hence from (B.2) :

$$\left( R_{n1+}^{10+} \right) = \frac{1}{Z} \frac{Z^4 n^4 (n-1)^{n-2}}{(n+1)^{n+1}}, \text{ and } \left( R_{n1+}^{10+} \right)^2 = \frac{2^8 n^7 (n-1)^{2n-2}}{Z^4 (n+1)^{2n+2}}. \quad (B.5)$$

Take  $\gamma_1' = l$ ,  $\gamma_2' = l-1$  in (5.3):

$$\begin{aligned} \left( R_{n,l}^{n'l-1} \right) &= \frac{Z^{2l} 2^{2l-1}}{n^{l+1} n^l} \frac{\sqrt{n+l} n' + l-1}{(2l)! (2l-2)!} \sqrt{\frac{(n-l)(n'-l+1)}{n-l} \frac{n'-l+1}{n'-l+1}} \times \\ &\quad [\{V\} - \{VII\} + \{VI\} - \{VIII\}] \\ &= \frac{Z^{2l} 2^{2l-1}}{n^{l+1} n^l} \frac{1}{(2l)! (2l-2)!} \sqrt{\frac{n+l} {n-l-1} \frac{n'+l-1}{n'-l}} [\text{Idem}] \quad . \quad . \quad (B.6) \end{aligned}$$

In the above put  $l=1$ ,  $n'=1$

$$\therefore (R_{n,1}^{10}) = \frac{Z^2}{n^2} \sqrt{(n+1)n(n-1)} [\{V'\} - \{VII'\} + \{VI'\} - \{VIII'\}], \quad . \quad (B.7)$$

where

$$\{V'\} = \int_0^\infty r^{\gamma_1'+\gamma_2'+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-2} \left(\frac{2Zr}{n}\right) dr, \quad \{\gamma_1' \rightarrow 1, \gamma_2' \rightarrow 0\}$$

$$\{VI'\} = \int_0^\infty r^{\gamma_1'+\gamma_2'+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-1} \left(\frac{2Zr}{n}\right) S_{2\gamma_2'+1}^1 \left(\frac{2Zr}{n}\right) dr; \{\gamma_1' \rightarrow 1, \gamma_2' \rightarrow 0\}$$

$$\{VII'\} = \int_0^\infty r^{\gamma_1'+\gamma_2'+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-2} \left(\frac{2Zr}{n}\right) S_{2\gamma_2'+1}^1 \left(\frac{2Zr}{n}\right) dr; \{\gamma_1' \rightarrow 1, \gamma_2' \rightarrow 0\}$$

$$\{VIII'\} = \int_0^\infty r^{\gamma_1'+\gamma_2'+1} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-1} \left(\frac{2Zr}{n}\right) dr, \quad \{\gamma_1' \rightarrow 1, \gamma_2' \rightarrow 0\}$$

Now, since  $S_{2\gamma_1'+1}^1 \left(\frac{2Zr}{n}\right) = 1 - \frac{2Zr}{n'} \frac{1}{2\gamma_2'+1}$  (See, I)  $= 1 - 2Zr$ ,

$$\{VI'\} = \{VIII'\} - 2Z \int_0^\infty r^{\gamma_1'+\gamma_2'+2} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-1} \left(\frac{2Zr}{n}\right) dr;$$

$$\{VII'\} = \{V'\} - 2Z \int_0^\infty r^{\gamma_1'+\gamma_2'+2} e^{-Z\left(1+\frac{1}{n}\right)r} S_{2\gamma_1'+1}^{n-2} \left(\frac{2Zr}{n}\right) dr.$$

Hence the expression within the parentheses of (B 7)

$$= 2Z \left[ \int_0^{\infty} r^{\gamma_1 + \gamma_2 + 2} e^{-Z \left( 1 + \frac{1}{n} \right) r} S_{2\gamma_1 + 1}^{n-2} \left( \frac{2Zr}{n} \right) dr \right. \\ \left. - \int_0^{\infty} r^{\gamma_1' + \gamma_2 + 2} e^{-Z \left( 1 + \frac{1}{n} \right) r} S_{2\gamma_1' + 1}^{n-2} \left( \frac{2Zr}{n} \right) dr \right]_{\gamma_1' = 1, \gamma_2' = 0} \quad (\text{B } 8)$$

$$= 2Z \left[ \frac{n-2! \Gamma(2\gamma_1' + 1)}{\Gamma(2\gamma_1' + n-1)} \left( \frac{n}{n+1} \right)^{\gamma_1' + 3} \frac{1}{Z^{\gamma_1' + 3}} \sum_{\tau=0}^{n-2} \binom{n-1}{n-2-\tau} \times \right. \\ \left. \frac{\Gamma(\gamma_1' + 3 + \tau)}{\tau!} (-)^{n-2-\tau} \left( \frac{n-1}{n+1} \right)^{\tau} - \frac{n-1! \Gamma(2\gamma_1' + 1)}{\Gamma(2\gamma_1' + n)} \left( \frac{n}{n+1} \right)^{\gamma_1' + 3} \frac{1}{Z^{\gamma_1' + 3}} \times \right. \\ \left. \sum_{\tau=0}^{n-1} \binom{n-1}{n-1-\tau} \frac{\Gamma(\gamma_1' + 3 + \tau)}{\tau!} (-)^{n-1-\tau} \left( \frac{n-1}{n+1} \right)^{\tau} \right] \quad (\text{B } 9)$$

$$\sum_{\tau=0}^{n-2} \binom{n-1}{n-2-\tau} \text{ has two contributions for } \tau = n-2 \text{ and } n-3,$$

$$\sum_{\tau=0}^{n-1} \binom{n-1}{n-1-\tau} \text{ has two contributions for } \tau = n-1 \text{ and } n-2.$$

$$(\text{B } 9) = \frac{4}{Z^3} \left( \frac{n}{n+1} \right)^4 \left[ 2n \left( \frac{n-1}{n+1} \right)^{n-3} - (n-1) \left( \frac{n-1}{n+1} \right)^{n-3} - (n+2) \left( \frac{n-1}{n+1} \right)^{n-1} \right] \\ = \frac{4}{Z^3} \left( \frac{n}{n+1} \right)^4 \left( \frac{n-1}{n+1} \right)^{n-3} \frac{4n}{(n-1)(n+1)} = \frac{2^4 n^3 (n-1)^{n-3}}{Z^3 (n+1)^{n+3}} \quad (\text{B } 10)$$

$$\text{Hence } \left( R_{n-}^{10-} \right) = \frac{1}{Z} \frac{2^4 n^3 (n-1)^{n-3}}{(n+1)^{n+3}}$$

$$\text{and } \left( R_{n+}^{10-} \right) = \frac{2^5 n^3 (n-1)^{n-3}}{Z^3 (n+1)^{n+3}} \quad (\text{B } 11)$$

From (5.4) we have, putting  $\gamma = l+1$ :

$$\left( R_{n+l+}^{n+l+1-} \right) = \frac{Z^{n+l+3} 2^{n+l+3}}{(n n')^{n+l+3}} \sqrt{\frac{n+l+1}{n-l-1}} \sqrt{\frac{n'+l+1}{n'-l-2l}} \times \\ [ (n-l-1) \{ \text{IX} - \text{XI} \} + (n+l+1) \{ \text{X} - \text{XII} \} ] \quad (\text{B } 12)$$

$$\text{For } n=1, l=0 \quad \left( R_{10+}^{11-} \right) = \frac{Z^{3,3}}{n^3} \sqrt{\frac{n'+1}{n'-2l}} [ \text{X}' - \text{XII}' ], \quad (\text{B } 13)$$



where

$$\{X'\} = \int_{\gamma \rightarrow 1}^{\infty} r^{2\gamma+1} e^{-Z\left(1+\frac{1}{n'}\right)r} S_{2\gamma+1}^{n'-1} \left(\frac{2Zr}{n'}\right) dr,$$

$$\{XII'\} = \int_{\gamma \rightarrow 1}^{\infty} r^{2\gamma+1} e^{-Z\left(1+\frac{1}{n'}\right)r} S_{2\gamma+1}^{n'-2} \left(\frac{2Zr}{n'}\right) dr.$$

Applying (A.5) as before we derive :

$$\{X'\} = \frac{2n'^4(n'-1)^{n'-1}}{Z^4(n'+1)^{n'+1}}, \{XII'\} = \frac{2n'^4(n'-1)^{n'-2}}{Z^4(n'+1)^{n'+1}} \quad (B.14)$$

Hence 
$$\left(R_{10+}^{n'1-}\right) = \frac{1}{Z} \frac{2^3}{n'^2} \sqrt{(n'+1)n'(n'-1)} [X' - XII']$$

$$= -\frac{2^4 n'^{7/2} (n'-1)^{n'-1/2}}{Z (n'+1)^{n'+1/2}}$$

and 
$$\left(R_{10+}^{n'1-}\right)^2 = \left(R_{n1-}^{10+}\right)^2 = \frac{2^8 n' (n-1)^{2n-1}}{Z^2 (n+1)^{2n+1}}$$

$$\left[ \left(R_{n1-}^{10+}\right) = -\left(R_{10+}^{n'1-}\right) \right] \quad (B.15)$$

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## INDEX TO VOLUME 13 (A)

**Alkali elements, partial pressures of atoms and molecules in saturated vapours of the (Bhatnagar), 233**

**Bhanage, S. S. See Desai and Bhanage**

**Bhatnagar, A. S. The partial pressures of atoms and molecules in the saturated vapours of the alkali elements, 233**

**Bhatnagar, A. S. The thermal ionization of sodium and potassium atoms, 243**

**Brij Basu Lal. The arms of a spiral nebula in resisting medium, I, 19.**

**Brij Basu Lal. On the theory of a spiral nebula, II, 28**

**Brij Basu Lal. The arms of a spiral nebula in resisting medium, II, 165**

**Brij Basu Lal. Formation of the arms of a spiral nebula, 179.**

**Cassia alata Linn. seeds, Chemical examination of (Singh and Tiwari), I, 111.**

**Chorghade, S. L. The crystal structures and the space groups of some aromatic crystals: I. Phloroglucinol dihydrate,  $C_6H_2(OH)_6 \cdot 2H_2O$ , 161**

**Chowla, Inder. On Waring's problem (*mod p*), 195**

**Cubic crystals, Lattice sums of (Misra), 275.**

**Desai, T. V. and Bhanage, S. S. The effect of H-ion concentration on the time of setting and viscosity changes during the setting of thorium arsenate gel-forming mixtures, 100**

**Differentiability of step functions (Shukla), 271.**

**Fluid motions (Ram Ballabh), 151.**

**Formulae in partitions and divisors of a number (Ziaud Din), 221.**

**Gupta, H. C. Two self-reciprocal functions, 37.**

**Gupta, H. C. Operational calculus and infinite integrals, 225.**

**Infinite integrals (Mohan), 171**

**Infinite integrals involving Whittaker's functions (Varma), 40.**

**Mehta, S. D. The time of setting and changes in H-ion concentration during the setting of nickel hydroxide gels formed by the addition of electrolytes to the nickel hydroxide sol, 78.**

**Misra, R. D. Lattice sums of cubic crystals, 275.**

**Mital, P. C. On self-reciprocal functions, 42.**

**Mohan, B. Some infinite integrals, 171.**

**Motion in incompressible fluid of variable density (Mukherji), I, 1; II, 135.**

Mukherjee, Santi Ram Motion in incompressible fluid of variable density, I, 1, II, 135

Nickel hydroxide gels, time of setting and changes in H-ion concentration during the setting (Mehta), 78

*Nigella sativa* seeds, chemical examination (Singh and Tiwari), II, 51.

Operational calculus and infinite integrals (Gupta), 225

Optically active compounds in the solid state, nature of racemic modifications of (Singh and Perti), I, 59.

Perti, O. N See Singh and Perti.

Phloroglucinol dihydrate, crystal structure and space group of (Chorghade), 261

*Pinus gerardiana* Wall seeds, chemical examination of (Singh and Tiwari), 120

Radial oscillations of a star (Sen), 184

Ram Ballabh. Fluid motions of the type  $\xi_1 = \lambda_1 u_1$ , etc, and  $\xi_2 = \lambda_2 u_2$ , etc, 151

Roche's model, radial oscillations of (Sen), 44.

Rotating cepheid (Sen), 159

Saksena, B D Structure of liquid  $PCl_5$ , 251.

Saran, B M and Singh, B K The chemical examination of the fruits of *Terminalia Belerica* Roxb · I The component acids of the fatty oil, 69.

Self-reciprocal functions (Gupta) 37 ; (Mittal), 42

Sen, H. K Radial oscillations of the generalised Roche's model, 44

Sen, H K The rotating Cepheid, 159

Sen, H. K. Large radial oscillations of a star, 184.

Shukla, P. D. On the differentiability of step functions, 271

Singh, B K. and Perti, O. N Studies on the nature of racemic modifications of optically active compounds in the solid state, I, 59.

Singh, B K. See Saran and Singh

Singh, B K and Tiwari, R. D Chemical examination of the seeds of *Nigella sativa*, Linn. (Magrel) : II. The component glycerides of the fatty oil, 54.

Singh, B. K. and Tiwari, R. D. Chemical examination of *Sphaeranthus indicus* Linn. I The component fatty acids and probable glycerides of the fatty oil, 88.

Singh, B. K. and Tiwari, R. D. Chemical examination of *Cassia alata* Linn I The component acids of the fatty oil from the seeds, 111.

Singh, B. K. and Tiwari, R. D. Chemical examination of *Pinus gerardiana* Wall. (The component fatty acids and the probable glyceride structure of the fatty oil from the seeds), 120.

*Sphaeranthus indicus* Linn, chemical examination (Singh and Tiwari), I. 88.

- Spiral nebula, arms in resisting medium (Brij Basu Lal), I. 19, II. 165, theory (Brij Basu Lal), II. 18, formation of the arms (Brij Basu Lal), 179
- Structure of liquid  $\text{PCl}_5$  (Saksena), 251
- Terminalia belerica* Roxb seeds, chemical examination of (Saini and Singh), 69
- Thermal ionization of sodium and potassium atoms (Bhatnagar), 243
- Thorium arsenate gel-forming mixtures, viscosity changes during setting (Desai and Bhauage), 100
- Tiwari, R D *See* Singh and Tiwari
- Varma, R S An infinite integral involving Whittaker's function, 40
- Waring's problem (Chowla), 195
- Ziaud Din, M On formulae in partitions and divisors of a number, derived from symmetric functions, 221



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